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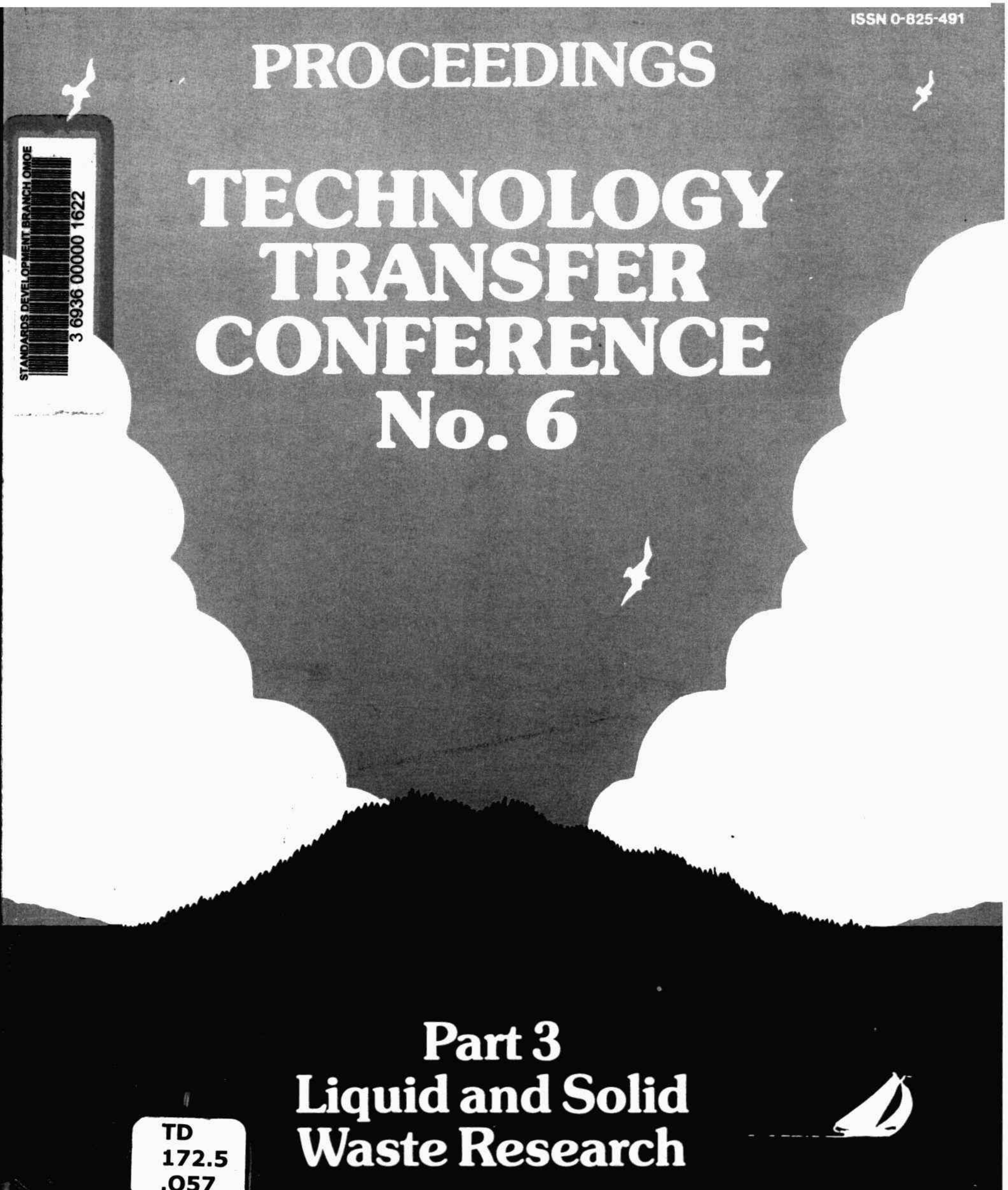

PROCEEDINGS

TECHNOLOGY TRANSFER CONFERENCE No. 6

Part 3
Liquid and Solid Waste Research

December 11 & 12, 1985
Toronto Hilton Harbour Castle

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PROCEEDINGS

TECHNOLOGY TANSFER CONFERENCE NO. 6

December 11 & 12, 1985

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PART THREE

LIQUD AND SOLID WASTE RESEARCH

Organized by
Research Advisory Committee

Sponsored by

Policy & Planning Branch
Ministry of the Environment
Ontario

STANDARDS DEVELOPMENT BRANCH
135 ST. CLAIR AVENUE WEST
TORONTO, ONTARIO M4V 1P5

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Goal Statement

"To achieve and maintain a quality of the environment - including air, water and land - that will protect human health and the ecosystem and will contribute to the well-being of the people of Ontario."

ACKNOWLEDGEMENTS

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INTRODUCTION

The Ontario Ministry of the Environment holds its annual Technology Transfer Conference to report and publicize the progress made on Ministry-funded projects. These studies are carried out in Ontario universities and by private research organizations.

The papers presented at Technology Transfer Conference No. 6, held in December 1985 are presented in Conference Proceedings. These Proceedings are divided into three parts corresponding to the conference sessions - Part 1 deals with air quality research, Part 2 with water quality research, and Part 3 with liquid and solid waste research. Papers dealing with analytical methods and instrument development are assigned to each of the three parts.

For further information on any of the projects, the reader is kindly referred to the Principal Investigators or to the Research Co-ordination Office at (416) 965-5788.

VOLATILE ORGANIC CARBON FROM LAND DISPOSAL OF WASTE - MECHANISMS OF EMISSIONS AND CONTROL STRATEGIES

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ABSTRACT

Organic wastes in solid and liquid form have been and will likely continue to be disposed of on or near the land surface. Disposal can take the form of treatment or storage. In mixture form, the individual chemical species exert some finite vapor pressure which ultimately can result in transport to the air. A review of vaporization mechanisms for waste in surface improvements, land farms and landfills will be presented. Models and experimental tests of control strategies will also be presented.

INTRODUCTION

Hazardous waste has been and will likely continue to be treated and disposed on land. As the waste resides on or near the land surface natural forces are continually in action to mobilize selected chemical constituents. These substances possess a range of pure component vapor pressures as characterized by vinyl chloride, which is a gas at ambient conditions, and Aroclor 1248, which is a liquid with a very low vapor pressure of 5E-4 atmospheres. Partials pressures, exerted when these substances are present in soil and water, play analogous roles in vapor emissions to air as chemical solubilities play is leachate emissions to groundwater.

SCOPE

This manuscript presents a review of selected technical literature on the mechanisms and models used to quantify the transport of volatile chemical species from land treatment operations.

The emphasis will be on the transport and emission of chemicals to the air. Emission sources will include surface impoundments, landfarm (or land treatment) and landfills. Currently available an "in-use" algorithm for estimating emissions will be presented as well as research trends in developing and validating better vapor emission models.

DEFINITION OF LAND TREATMENT/DISPOSAL OPERATIONS

Land treatment/disposal is a generic term that involves hazardous waste operations in, on and near the air-soil interface. Three specific operations are of interest in this manuscript.

A surface impoundment is a treatment and /or storage device of earthen construction containing hazardous waste in an aqueous phase. A liquid interface is in direct contact with the air phase. Although water is the predominant substance in the impoundment some organic or oil film may float on the surface and solid sludge exist on the bottom. The volatile components may exist in all three phases and encounter different transport pathways as it moves into the overlying air. The treatment operations usually occurring in surface impoundments is usually biochemical oxidation, however other reactive operations including neutralization (i.e., pH adjustment) are also performed. Impoundments are also used for temporary storage of wastewater either prior to or following other treatment operations. Water evaporation does not have to occur for chemical volatilization to occur.

The use of the upper soil zone to manage waste has been referred to as land spreading, land farming, sludge farming and more recently land treatment. The process itself is a natural one involving applications of appropriate waste to the soil surface, cultivation of the surface to bring aerobic bacteria into contact with the waste to affect chemical degradation processes. Industrial waste treated in this fashion contains numerous chemical species that are volatile and considered hazardous. The active zone for biochemical reactions and volatilization processes is the few inches near the air-soil interface.

Landfills are a well known receptor of hazardous waste. These choices are aimed at long-term waste storage. Early versions of these subterranean enclosures, that received waste, were referred to as burial, trenches, pits and "hole in the ground." The more recent versions are but minor improvements over the earlier models and constitute a form of a capsule for slow,long term chemical release to both groundwater and the air. It would appear that volatile chemical emissions on a unit surface are a basis, would be high for surface impoundment, intermediate for landfarming and lowest for landfills. This preception is based upon the fact that surface impoundments are liquid and reside on the surface, landfarms involve soil layers and landfills are well below the soil surface. As a consequence, the chemical vapor transport pathway seems to lengthen and otherwise become more difficult. The concentration of chemicals involved in the three operations tend to nullify this trend.

Typically the chemical concentrations in surface impoundments are in the part per million range. Concentrations can be as high as 10 to 20% (wt. basis) on landfarms and in landfills. The following section will contain a presentation of each of the three operations separately. The individual chemical vapor transport processes will be described.

VOLATILES FROM SURFACE IMPOUNDMENTS

In the first case of volatile emissions from surface impoundments the chemical species are assumed to be in solution in the aqueous phase. The maximum concentration, in the case of pure components, is controlled by the solubility of the chemical in water. In the case of mixtures the solubility is controlled by the activity coefficient which accounts for the presences and influence of the other chemicals in solution. The influence of mixture properties should be accounted for when the total concentration of all species approaches ~5% (wt). Chemical solubility and activity coefficient prediction methods are contained in Reid, Prausnitz and Sherwood (1977), Lyman, et. at. (1982) and Dean et. al. (1984). The latter work emphasizes the application of the methodology to hazardous waste in land pollution scenarios.

The equilibrium concentration in air is traditionally quantified by Henry's constant. Henry' constants are only valid for single components in aqueous solution and normally do not account for th mixture conditions which are usually present in surface impoundments. In reality the Henry's constant contains the activity coefficient so that the techniques noted above can be used to specify the air-water equilibrium relationship for mixtures. The larger the Henry's constant the more volatile the substance. This is a thermodynamic quantity and only quantifies the relative potential for volatile loss from water.

Evaporation rate equations for chemicals from surface impoundments were first quantified by Thibodeaux and Parker (1976) for alcohols, aldehydes and soluble acids. The same mehtodology applies to hazardous substances in waterbodies (McKay an Leinonen, 1975; Liss and Slater, 1974). A readable presentation on vaporization of chemicals from all types of waste bodies in contained in Chemodynamics (Thibodeaux, 1979). For substances in solution the well known two-resistance theory applies. This concept combines the turbulent diffusion transport resistances that the volatile molecules encounter on the water side and air side of the interface plus the equilibrium potential (i.e., Henry's constant). A single, transport coefficient results which when combined with the concentration in water yields a first order rate equation that quantifies the chemical emission rare in mass per time per unit surface area. A report by Thibodeaux, Parker and Heck (1982) presents the necessary algorithms for estimating emission rates.

Field measurements aimed at verification of the two-resistance model is also contained in the above report. The field measuring technique is a concentration profile (CP) mehtodology based on obtaining concentrations within the turbulent boundary (air) layer. This together with velocity and temperature profiles in the same zone and the flux computation formula yields the volatilization rate from the water surface. Hwang and Thibodeaux (1983) developed a modification of the CP methodology which reduces the data required significantly. Recently manuscripts by Thibodeaux, Parker, Heck (1984) Thibodeaux, Springer, Lunney, James, Shen (1982), and Springer, Thibodeaux, Lunney, Parker, James (1983) give field emission rate for methanol, acetone, total hydrocarbon (FID), benzene, toluene, 1,1 trichloroehtane, total chlorinated hydrocarbons and methylene chloride.

Current research activities are aimed at increasing the robustness of the two-resistance model and techniques for reducing and controlling the emission from surface impoundments. General techniques have been available for estimating mass-transfer coefficients at the air-water interface of waterbodies. Efforts are underway to quantify coefficients with specific application to the unique environment of surface impoundments. Lunney, Springer and Thibodeaux (1985) report on studies of the effect of impoundment fetch-to-depth ratio of the liquid phase mass-transfer coefficient. Wind has a significant effect on the magnitude of the transport coefficient on either side of the interface. In the absence of wind warm water provides the motive force for maintaining volatile emission at a relatively high rate. Pilot scale simulations have yielded alorithms to estimate volatile chemical emission rates in the absence of wind when the water is warmer than the overlying air (Springer, Thibodeaux and Hedden, 1984).

Control methods for volatiles from surface impoundments have been proposed and there are several possible techniques that can be used to reduce emissions (Cudahy and Sandifer, 1980). The control methods fall into three general categories: covers, fences and sorbents. Covers involve the placement of a barrier at the water-air interface. Oil (slicks) layers, plastic films, mats of floating materials and foams have been proposed. Fences, both perimeter and surface networks, have been proposed to partially nullify the wind enhanced volatilization. On bottom or suspended sorbents (liquid droplets and solid particles) have been proposed as a means of retarding the evaporation by reducing the effective concentration in the water.

Parker (1984) performed pilot scale wind tunnel experiments with ethyl ether to investigate the effect of fences in deducing volatile emissions from surface impoundments. A perimeter fence of solid construction (i.e., non-porous) can give up to approximately 40% volatile reduction. A network grid can give up to 80% reduction as can a porous perimenter fence (Thibodeaux, Springer and Parker, 1985).

If there are no competitive pathways for the fate of the volatiles in the impoundment such as biochemical degradation, hydrolysis, etc., then the use of fences will not reduce the quantity of volatiles ultimately emitted through the surface. The only benefit in the case will be to reduce the high rates of emission to lower values for a longer period of time. However, if degradation processes are present within the water or the sediment the fences force the volatile constituents to remain in the water for longer time periods allowing more efficient destruction or conversion reactions.

Laboratory investigations of floating oil barriers, used both in the absence of and presence of wind, to reduce emissions have been completed (Springer, Valsaraj and Thibodeaux, 1985). Lauryl alcohol, octyl alcohol and mineral oil were used as floating "oil" covers in the studies with acetone and benzene. It was found that the control methods examined could be highly effective in reducing emissions if properly employed. Benzene emissions were reduced by 53% with an oil layer of 5.6 mm. Acetone and n-propanol were reduced by 68%. Although the floating oil may reduce VOC emissions it will also restrict contact between the air and water, thus reducing the rate at which oxygen can enter the water.

VOLATILES FROM LANDFARMING

Organics on or near the soil surface are readily volatilized into air. The studies performed by soil scientist on the volatile transport of pesticides applied to soil surfaces has direct application to land treatment of organic and petroleum waste sludges and liquids.

The first attempt at developing a simple mathematical model for assessing the volatilization flux rate of organic chemicals from landfarming operations was made by Thibodeaux and Hwang (1982). The model employed the lumped parameter concept of mathematical approximations in order to develop an algorithum that quantified some of the major physico-chemical processes of chemical evaporation from soils. Some major shortcomings of the model is that it ignores the contribution of water and thermal effects on the chemical evaporation and transport process. Recent laboratory investigations have verified major components of the landfarm model. Carvanos, et. al. (1985) report experimental results using benzene, carbontetrachloride and trichloroethylene with clay, sand and organic loam soils. The ratio of actual to theoretical emission rates from the soil surface ranged 0.84 to 2.01. In general the actual emission rates were greater than the predictions of the model equation.

The vaporization of chemicals from soils is a very complicated process. The process associated with pertroleum landfarms is likely simpler than pesticide evaporation. The equilibrium relationship in the case of volatiles in oily sludges, is Raoult's law. In the example of benzene, it is assumed that Raoult's law can be used to quantify the partial pressure in the air filled pores of the soil. Desorbed molecules of benzene move upward (and downward) by diffusion in the vapor phase. The diffusion coefficient need account for the tortousity of the pathway through the soil pores. As the molecules move through the final pores, located at the soil-atmosphere interface, an air-side resistance must be overcome before the molecule enters the turbulent atmospheric boundary layer. Available transport coefficients for this layer have been reviewed recently by Scott and Thibodeaux (1984).

A recent series of papers on the behavior of trace organics in soils by Jury, Spencer and Farmer (1983-84) contain excellent reviews of the vaporization processes and models for pesticides on soils. Two up-published thesis (Carvanos, 1984 and Buff, 1984) report on evaporation processes of high chemical concentration more nearly applicable to landfarms and contaminated land cases.

VOLATILES FROM LANDFILLS

At least 100 volatile chemicals in fairly high concentration and well above the odor threshold have been identified in landfill gas (Young and Parker, 1983). Farmer et. al., (1980) were the first group of researchers to propose a model for calculating the flux rate of chemical vapors from a landfill source. The model involved hexachlorobenezene and was based upon Fick's first law of molecular diffusion. Thibodeaux (1981) extended the diffusion concept to account for convective effects caused by bio-gas generated within the cells. Both models consider the landfill cap to be the major vapor diffusive barrier in steady-state analysis. An additional modification of the convective/diffusive model accounted for the transient behavior of the transport phenomena as driven by fluctuations in atmospheric pressure (Thibodeaux, et. al., 1982).

Pilot-scale laboratory simulations are underway to test the proposed convection/diffusion models. For some, yet unresolved, reason the experimental flux rate is exceeding the model predicted flux rates by a large factor. So it can be said this time that the existing predictive models for vapors from landfills underestimate the actual emission rates (Thibodeaux, Springer, Hilderbrand; 1984).

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HAZARDOUS ORGANIC CHEMICALS IN GROUNDWATER AT ONTARIO LANDFILLS

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Key words: Hazardous Organics, Organics, Groundwater, Landfill.

ABSTRACT

Research in 1984/85 has concentrated on the occurrence and migration of organic contaminants at three landfill sites to determine the hydrogeological, geochemical and microbiological controls on the contaminant distributions. The North Bay and Woolwich plumes occur in stratified sands and the New Borden plume occurs in sandy silts. Emphasis has been placed upon the relatively mobile organics at these sites, namely chlorinated one- and two-carbon compounds and monoaromatics (benzene and substituted benzenes).

The New Borden plume extends laterally about 150 m from the site and trace organic contaminants extend, rather sporadically, throughout at least 100 m. Concentrations are temporally variable. Individual organics are usually less than 1 ppm in the landfill and less than 100 ppb in the groundwater.

Temporally and spatially variable organic distributions characterize the other plumes as well. Identifying the cause of this variability is the current emphasis at these sites. Variable input of contaminants from the landfill to the groundwater system exerts a major, but not exclusive, control. Detailed coring has been undertaken with the development of a reliable coring method. This permits the detailed hydrostratigraphic/hydrogeologic studies required to evaluate the influence of variations in flow patterns upon the organic distributions. The contributions of variable sorption properties and biodegradation rates to the variability in contaminant distribution are also being evaluated.

In addition, some unexpected biotransformation is suspected within the plume at North Bay. Anaerobic degradation of xylenes and trimethyl benzenes is apparent, for example, and so biotransformation processes are being evaluated with representative laboratory experiments.

ORGANIC CONTAMINANTS IN GROUNDWATER AT FOUR ONTARIO LANDFILLS

SOME PRELIMINARY OBSERVATIONS

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ABSTRACT

Studies of the migration of organic contaminants in shallow aquifers impacted by landfill leachate are continuing at seven sites in Ontario. Some results from four sites, three located on very permeable sand deposits and one one less permeable sand till, are presented. The migration rate and persistence of volatile, one-and-two carbon, halogenated hydrocarbons (halocarbons) and volatile aromatic hydrocarbons are emphasized. The compounds are ubiquitous in sanitary landfill leachates and are quite mobile in groundwater. They are at very low concentrations (less than 5ppb each) at the Borden landfill site, where most waste was burned before landfilling.

At the Woolwich site, volatile halocarbons are found at very low concentrations (less than 0.2ppb each) up to one kilometer from the site, indicating that they may be very mobile and persistent in this aquifer. Attenuation, probably due mainly to dispersion, has resulted in only sub-ppb concentrations persisting beyond two hundred kilometers of the site.

The contaminant plume at North Bay has been discharging to the surface about eight hundred meters from the site for a number of years. Some mobile volatile organics, therefore, are found throughout the plume. Halocarbons do not persist and some aromatics appear to be undergoing biodegradation as well. For these and other contaminants, dramatic attenuation is observed within the eight hundred meter plume, probably as the result of dispersion.

Groundwater velocities in the less-permeable sand and sand till at the new Borden site are much lower than in the other aquifers, so contaminants have only migrated perhaps two hundred meters laterally. Volatile halocarbons may be migrating at the groundwater velocity, while some retardation of aromatics may be occurring. However, the erratic contaminant distribution complicates the consideration of contaminant migration.

Temporal variations, over weeks and years, are found for all contaminants at these sites. Input from the landfill appears to be temporally variable and so is a major cause of subsequent variations within the leachate plume. The processes of dispersion, which smoothes such variations at some sites (Borden), does not appear to be effective at damping temporal variability along the plume at North Bay. Current studies are addressing the temporal variability in the North Bay plume in order to facilitate interpretation of organic contaminant distributions.

INTRODUCTION

It has long been recognized that municipal landfills in Ontario and elsewhere produce leachate that causes contamination of groundwater. Zones of contaminated water, termed leachate plumes, can be quite extensive at landfills situated on permeable, geological materials. Since 1976 researchers at the Institute for Groundwater Research have investigated the physical and chemical controls of contaminant migration at such landfill sites. Since 1982 additional emphasis has been placed on the migration of organic contaminants. Some of these organic studies were conducted in collaboration with researchers from the Environmental Engineering Group at Stanford University and from the Department of Environmental Chemistry and Biology at the Oregon Graduate Center.

Six landfill sites and one industrial waste disposal site are currently being investigated. Three sites (Borden, Woolwich, North Bay) are situated on unconfined sand aquifers, one site (new Borden) on unconfined sand and clay tills, and two sites (Bayview and Hamilton) on fractured sedimentary bedrock. The Tricil waste disposal site is in less-permeable clay and clayey-till. Thus, a wide range of hydrogeological conditions are included in these studies.

Methods of investigation at these sites are summarized by Barker et.al. (1984). Essentially, an extensive network of multilevel groundwater sampling devices, termed multilevel piezometers, are established to provide a detailed, three-dimensional picture of contaminant distributions. Hydraulic information obtained by water-level measurement, well-testing, and detailed core analysis defines the groundwater flow system responsible for contaminant migration. Hydraulic testing, piezometer sampling , and laboratory studies of sorption and biotransformation can then be integrated, with the assistance of mathematical simulation and modeling when appropriate, to describe the migration of organic contaminants in the plumes.

With respect to organic contaminants, these studies are addressing several questions: 1) what organics are present in landfill leachates? 2) how fast do they migrate in groundwater? 3) how far and for how long do they persist?

and 4) what are the processes controlling their migration and persistence? The fourth question is important to address if the results of these field studies are to be generalized for application to other landfill or waste disposal situations. Only a thorough understanding of the processes will establish a reliable predictive capability.

It is important to study real landfill situations since only in the field are the results of complex, interactive transport processes fully apparent. This complexity, however, also limits our ability to identify the contribution of specific processes, such as sorption, dispersion, and transformation, to organic contaminant migration and persistence. The major field limitations are the undefined history of inputs from the waste to the groundwater and the uncertainties in the flow system hydraulics. Laboratory studies, under conditions representative of field sites, are often more useful to evaluate specific processes. Another approach currently being emphasized at IGR is to conduct field-scale experiments in which solute-spiked groundwater is injected into a well-characterized aquifer and the migration of solutes under natural flow conditions is monitored by sampling from a dense, three-dimensional network of multilevel piezometers. This provides for a well-defined input and a well-characterized flow system in which the processes can be more clearly investigated. "Natural gradient injection" experiments were used by Sudicky et.al.

(1983) to study dispersion of chloride, by MacKay et.al. (1983) for selected halogenated organics, by Sutton and Barker (1985) for selected soluble organics, and by Patrick and Barker (in press) for monoaromatic hydrocarbons. Thus, laboratory and field-scale experiments augment the current studies of organic contaminant migration at landfill sites, all with the aim to better understand the processes controlling organic contaminant behaviour in groundwater.

This paper describes some of the current studies at the four landfill sites in sand and sand till deposits. It is impractical to examine the distribution of the forty to one hundred organics commonly identified in landfill leachate, especially considering the need to analyze groundwaters from thirty to one hundred points to adequately define their spatial distributions. Therefore, at each site a detailed characterization of landfill leachate was conducted and specific organics were selected for more detailed study. To date, these studies have emphasized commonly encountered, more mobile organics which can routinely and reliably be determined in numbers sufficient to provide accurate "snapshots" of their distribution in groundwaters. These distributions are then interpreted in terms of the hydrogeological processes (advection, dispersion) and geochemical processes (sorption, chemical and microbial reaction) which must control the distributions. These well-characterized sites can be used in the future to examine the migration of less-mobile organics of particular environmental concern.

In the context of the above rationale, landfill studies to date have emphasized two classes of volatile organic contaminants: 1) halogenated, one-and-two carbon hydrocarbons which are common industrial chemicals that regularly occur in household products, and 2) aromatic hydrocarbons, occasionally chlorinated, that are common in petroleum products and other industrial chemicals as well as in household products.

The specific organics considered are listed in Table 1. Other organics commonly encountered in landfill leachate plumes are discussed by Reinhard et.al. (1984). This paper will emphasize the mobility and persistence of these organics relative to indicator parameters, such as chloride (Cl^-) and non-volatile, dissolved or colloidal organic carbon (TOC), which are considered to migrate at the same velocity as the groundwater and, in the case of Cl^-, are not sorbed nor transformed.

BORDEN

Studies of the hydrogeology and inorganic geochemistry of the leachate plume from the CFB Borden abandoned landfill culminated in the special issue of the Journal of Hydrology (vol. 63 no. 1/2, 1983). Selected piezometers were sampled for organic contaminants. Results pertinent to this study are summarized in Table 1 and the total volatile halocarbon concentrations are shown in Figure 1.

The plume is migrating in an unconfined aquifer in stratified sands. The chloride plume, shown in cross-section in Figure 1, shows some effect of input concentration fluctuation, but clearly indicates the dilution in the flow direction attributed to dispersion.

The concentration of volatile organic contaminants in these groundwaters is very low (Table 1) and, if well P-3 is considered background, hardly above background levels. At this landfill most of the refuse was burned during operations from 1940 to 1973 before normal landfilling operations were employed from 1973 to 1976 when site was abandoned. The lack of volatile organics is attributed to this operation history, while possible biotransformations under the methanogenic conditions within the site and hydrodynamic dispersion are probably of secondary importance.

WOOLWICH

The trace organics found in groundwater at the Woolwich landfill site near Waterloo have been discussed by Reinhard et.al. (1984) and selected data from a highly-impacted groundwater are presented in Table 1. Although established on sand deposits, landfilling has been conducted in large trenches, seven to ten meters above the water table, since the mid-1960s. In detail, the contaminant distribution, even near the landfill, is complex and irregular, with the upper part of the water table aquifer highly contaminated near the site and the contaminated zone becoming more erratic and deeper in the aquifer as it migrates south and southeast from the site. Figure 2 uses the maximum chloride value at each multilevel piezometer to define the lateral extent of the plume in 1984. In its three-dimensions, the plume is less regular than Figure 2 indicates.

Zapico (M.Sc. thesis, in progress) developed a coring technique to obtain representative cores of the aquifer. Detailed profiling of hydraulic conductivity over five to ten centimeter lengths of core is underway, as is an evaluation of borehole and piezometer hydraulic testing in order to provide an improved definition of the site hydrogeology--a basic requirement for the interpretation of organic contaminant distributions. Initial assessment of hydraulic conductivity and gradients (water-table configuration) suggests that conservative leachate tracers, such as Cl^- should be moving fifty to two hundred and fifty meters laterally each year. Given the twenty year landfilling history, the chloride plume should extend beyond the limits of Figure 2, whereas the plume becomes poorly defined after five hundred meters. Either the hydraulics are incorrectly perceived or the dilution by dispersion is sufficient to obscure the plume front. The multilevel piezometers where more than 0.5ppb total volatile halocarbons were detected in any of the samplings from 1982 to 1984 are circled in Figure 2. The tentative identification of these organics beyond the well-defined Cl^- plume front suggests that very diluted leachate has migrated more than one kilometer from this site. This problem is being addressed by Zapico.

In terms of the volatile halocarbons and aromatics listed in Table 1, the Woolwich plume has a slightly different mix of contaminants compared to the other sand aquifer plumes. Trichloroethylene dominates the halocarbons and 1, 2, 4-trimethylbenzene is in lower concentration. This could relate to landfill composition or to unique geochemical processes active at this site. Such speculations may be better addressed when the hydrogeology is better understood.

NORTH BAY

The most intensively studied landfill site is at North Bay, Ontario (Reinhard et.al., 1984; Barker et.al., in press). The landfill lies in a complex deposit of bedded glaciofluvial sands underlain by gneissic bedrock. The site has operated since 1962 and leachate-contaminated groundwater has been observed discharging near a creek, about eight hundred meters from the landfill, since our studies began in 1980 (see Figures 3 and 4). Thus, at this site we have not been able to discuss a plume front, as at the other sites. This study, therefore, cannot deal with relative velocities of contaminants, but rather provides field evidence of contaminant attenuation and persistence during transport in anoxic groundwater.

The organic geochemistry of the leachate is presented by Reinhard et.al. (1984) and Barker et.al (in press). Table 1 presents an analysis of a highly impacted groundwater pertinent to this discussion. Volatile halocarbons do not persist throughout this plume, probably due to their biotransformation under the methanogenic conditions of this plume. Volatile aromatics are more persistent, however, and are found in the discharge zone, although at significant attenuation.

Recent hydrogeological studies (M. Moore and N. Gensky, M.Sc. theses in progress) have identified a surprisingly uniform stratigraphy in the subsurface (see Figure 5) which contrasts sharply with the complex, fluvial sands apparent above the water table. A relatively thick sand of rather uniform appearance and hydraulic conductivity (about 1×10^{-2}cm/s) may extend throughout the flow system. Average groundwater velocities appear to be from 4×10^{-4} cm/s to 1×10^{-3} cm/s. Unretarded contaminants could, therefore, be moving through the 900 meter long flow system within two to four years. This is more than twice the velocity calculated from earlier, less extensive studies.

Recent geophysical studies by Greenhouse have elucidated the bedrock control over part of this plume's distribution and have identified smallscale structures in the sands near location API (Figure 6). The relationship of these structures to the hydraulic conductivity profiles is being studied. They have also shown that ground pentrating radar (GPR) can accurately define the lateral extent of the leachate plume in this area. Thus, the North Bay plume is providing an excellent evaluation of geophysical techniques proposed for use in contaminant hydrogeology studies.

Spatial and temporal variability of contaminant distributions have been the focus of recent studies. Figure 5 indicates vertical variability in hydraulic characteristics and selected contaminant distributions at piezometer G, adjacent to the landfill, and at piezometer LL, about five hundred meters down-gradient. Vertically, the chloride and ethyl benzene co-vary, with the highest concentrations found in the fine-medium sand, the unit which conducts the major flux of leachate. Figure 7 demonstrates the temporal variability (May to September, 1985) of contaminant and leachate-indicators chloride and total organic carbon (TOC) at single sampling points from each site (LL-9, G-5). Data collection is continuing and will be combined with data from 1982 onwards in a rigorous evaluation of temporal variability and its causes. However, the temporal variability shown for LL-9 (for all compounds except chlorinated benzene) is greater that for G-5. The dominant source of temporal variability is probably the variation of contaminant inputs from the landfill, although selective biotransformation and hydraulic flow changes could also be significant causes. Given the input variability as the source for variability at G-5, located beside the landfill, it was anticipated that the process of dispersion would bring about more even contaminant distributions over time at piezometer LL. Dispersion is considered a major agent for the generation of the attenuated but "smoothed" contaminant distributions of the Borden plume (MacFarlane et. al. 1983). At Borden, the major source of dispersion is likely the small-scale (10 cm to 2 m) hydraulic heterogeneities of the sands. Although there is excellent geophysical evidence for small-scale layering at North Bay, the hydraulic conductivity distributions, indicated in Figure 5, appear much more homogeneous than at Borden. This suggests that dispersion may be less significant in the North Bay plume and may account for the persistence of temporally-variable contaminant distributions along the plume.

The apparently variable contaminant input to the flow system and this persistent variability in the plume at North Bay precludes direct, simple evaluation of contaminant distributions to assess chemical or biological processes that may remove certain contaminants. Barker et.al. (in press) considered the fate of selected organics that co-vary at the start of the plume (piezometer G), probably reflecting a covariance in their input to the system. By examining the distribution of covariant pairs of organics at piezometers along the eight-hundred-plus meter plume, the relative persistences were evaluated. All xylene isomers appeared to be biotransformed more rapidly than ethylbenzene, while 1, 2, 4-trimethylbenzene was removed faster than was 1, 4-dichlorobenzene. These observations are not consistent with the general expectation of non-biodegradability of substituted benzenes under the anoxic conditions of this plume (Wilson and MacNabb, 1983), but the persistence of the dichlorinated benzene, relative to the trimethylbenzene, is perhaps consistent with the enhanced persistence of chlorinated benzenes, relative to the methyl-substituted benzenes (Kuhn et.al. 1985, for example). Kuhn and co-workers also report the biotransformation of xylenes under anaerobic conditions.

Studies at the North Bay site are continuing, but the emphasis is being placed on the definition and explanation of the temporal and spatial distributions of contaminants. This site will also provide a strictly anaerobic site for future controlled field studies similar to those underway in an aerobic segment of the Borden plume.

NEW BORDEN

The new landfill at CFB Borden consists of a series of excavated cells about one hundred and fifty meters by sixty meters, which, starting in 1976, have been filled with municipal refuse and covered. Two cells have been completed and the third is partially full. These cells are excavated into a sequence of fine sand, silty sand till and clayey silt till (figure 8).

Hydraulic conductivities are in the rate of 10^{-3} to 10^{-6} cm/s for the silty sand till with a representative average of 5 x 10^{-5} cm/s, so contaminant migration should be limited at this nine year old site to shallow depths within one hundred and fifty to two hundred meters of the cells.

Carey (1985) details the hydrostratigraphy and northward-extending plume pattern as defined by chloride (Cl^-) and aqueous, non-volatile organic carbon (TOC). Monitoring on three occasions in 1985 emphasized the Cl^-, TOC, and volatile aromatic contaminants. Table 1 presents some pertinent results for leachate at this site. A south to north cross-section is presented in Figure 8, indicating the distribution of chloride and two volatile organics, toluene (C_7H_8) and carbon tetrachloride (CCl_4) These plumes are contoured using the chloride plume for 1984 obtained by Carey (1985) as a model although the organic contaminant occurrences are somewhat erratic. For example, upgradient (south) from the landfill, significant chloroform was found in piezometers at M14, while chloride and toluene levels were very low--perhaps at background levels.

This erratic, trace organic distribution makes the discussion of organic mobility relative to the conservative tracer Cl^- difficult. Chloride and carbon tetrachloride have both reached M18 at somewhat reduced concentrations. Toluene has reach B84-13 and may also have reach M17. This would indicate carbon tetrachloride is as mobile as chloride, while toluene is slightly less mobile. Since these organics are slightly hydrophobic, but of similar hydrophobicity (for example, their octanol-water partition coefficients are both about four hundred to six hundred), they both would be expected to be retarded somewhat with respect to chloride (Karickhoff, 1984). The fact that this expectation is not apparently met could be due to a number of factors, including 1) a low sorption potential of the porous media, 2) spatial and temporal variability in their inputs to the flow system from the landfill, and 3) biotransformation of toluene causing its greater apparent retardation. A more comprehensive view of contaminant distributions is clearly required and current studies at this site should provide a clearer description of contaminant migration.

COMPARISONS, GENERALIZATIONS, AND CONCLUSIONS

Volatile halocarbons and aromatic hydrocarbons are ubiquitous in leachate produced from landfilled, normal municipal refuse. However, where refuse has been burned (Borden) much lower concentrations are found. The concentration of particular organics in leachates varies widely from landfill to landfill, probably reflecting the specific hydrogeological and microbial/ geochemical conditions within the landfill as well as the particular materials landfilled. Where toxic wastes or industrial wastes are co-disposed with municipal refuse, much higher concentrations of these organics may be found in contaminanted groundwaters (Jackson et.al., 1985, for example).

Where landfill leachate impacts shallow, unconfined sand aquifers these organics appear to have migrated about as far as non-reactive, conservative tracers such as chloride. This indicates that sorptive retardation is minimal in sand aquifers such as Woolwich and North Bay, probably reflecting the dearth of solid organic matter, the major sorbant for organics, in such aquifers. Even in the sand till of the new Borden site, where organic matter may be more abundant, carbon tetrachloride appears to have migrated as far as chloride although the aromatic hydrocarbon toluene does not appear to have travelled as far. This apparent attenuation of toluene could reflect greater sorptive retardation, more biodegradation, or a different input history for the aromatics relative to chloride and carbon tetrachloride.

In all contaminated aquifers, the attenuation of organic contaminants along the flow system has been dramatic. High organic concentrations near the landfill give way to much lower concentrations within one hundred to five hundred meters. This attenuation is due primarily to dilution by dispersion, but biodegradation contributes in the case of some organics. For example, the decrease in volatile halocarbons and certain volatile aromatics at the North Bay site has been attributed to biodegradation under strictly anaerobic conditions (Barker et.al, in press). It is likely that anaerobic transformations occur in almost all landfills and their leachate plumes, but it is not possible at this time to confidently predict the resultant attenuation of organic contaminants.

Temporal variability of contaminant concentrations in landfill leachate plumes is significant. The major contribution is probably the temporal variability of contaminant input from the landfill. Dispersion should dampen temporal variability, but at North Bay in particular temporal variability persists through the flow system. The problem of temporal variability must be addressed in order to establish a scientific basis for designing groundwater monitoring programs. On the other hand, studies of the changes in temporal variability along groundwater flow paths may contribute to our understanding of the process of dispersion. In any event, the temporal variability problem must be addressed to facilitate the interpretation of the organic contaminant distributions in the North Bay plume.

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Table 1: Representative, Highly Impacted Groundwater from Landfill Sites in Southern Ontario

Landfill	Borden	Woolwich	North Bay	N.Borden
Piezometer	77-6-2	ML-06-2	G-5	84-2-1
Date	11/11/82	16/9/85	3/5/85	20/8/85
Chloride (mg/l)	103	1040	202	550
TOC (mg/l)	43	6490	145	294
Volatile Halocarbons (mg/l)				
Chloroform	0.1	3.0	<MDL	<MDL
1,1,1-Trichloroethane	<MDL	0.1	0.14	0.1
Carbon Tetrachloride	0.1	<MDL	<MDL	8.0
Trichloroethylene	0.29	21	<MDL	<MDL
Tetrachloroethylene	<MDL	<MDL	<MDL	8.0
Volatile Aromatics (mg/l)				
Benzene	3	9.1	45	8.5
Toluene	0.2	320	2.4	730
Ethylbenzene	0.2	12	58	13
Chlorobenzene	0.2	3	10	<MDL
Pr-plus p-xylene	0.2	28	94	27
O-xylene	0.2	22	12	40
1,2,4-Trimethylbenzene	0.2	<MDL	53	14
Napthalene	0.2	19	21	63

<MDL -- less than the method detection limit

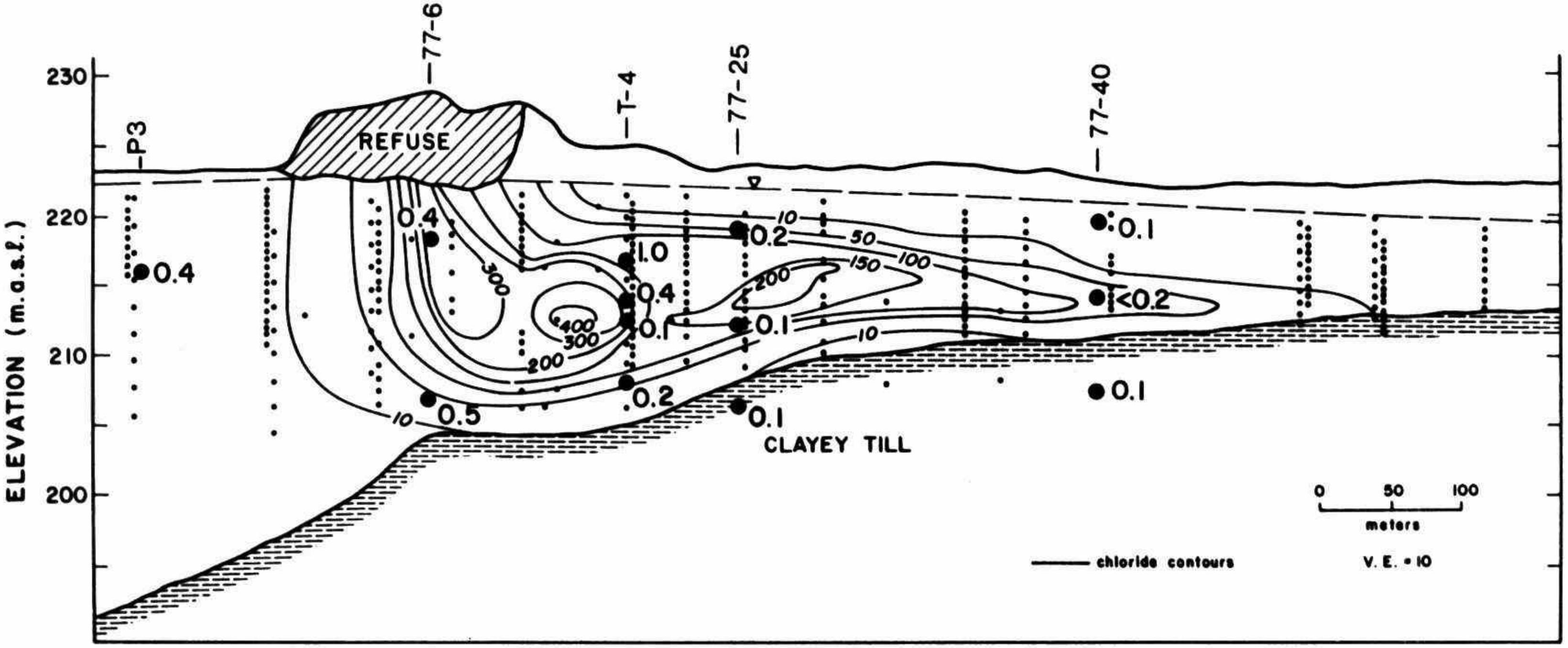


Figure 1. Cross-section through the abandoned Borden landfill showing the distribution of chloride (contoured) and the total volatile halocarbons, January, 1982.

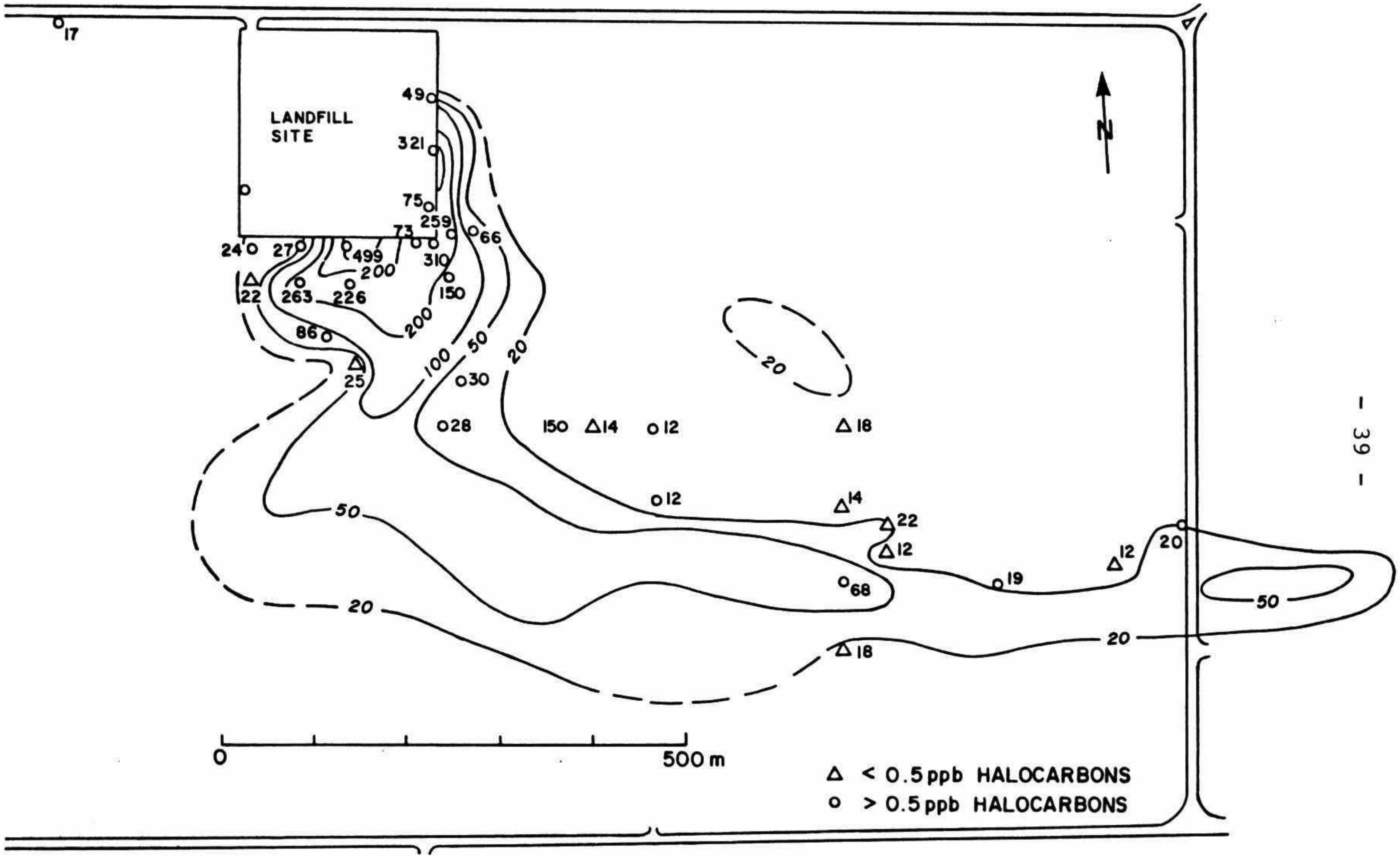


Figure 2. Plan view of the landfill-leachate plume at the Woolwich site. The maximum chloride concentration at each multilevel is contoured and occurrences of significant volatile halocarbons indicated.

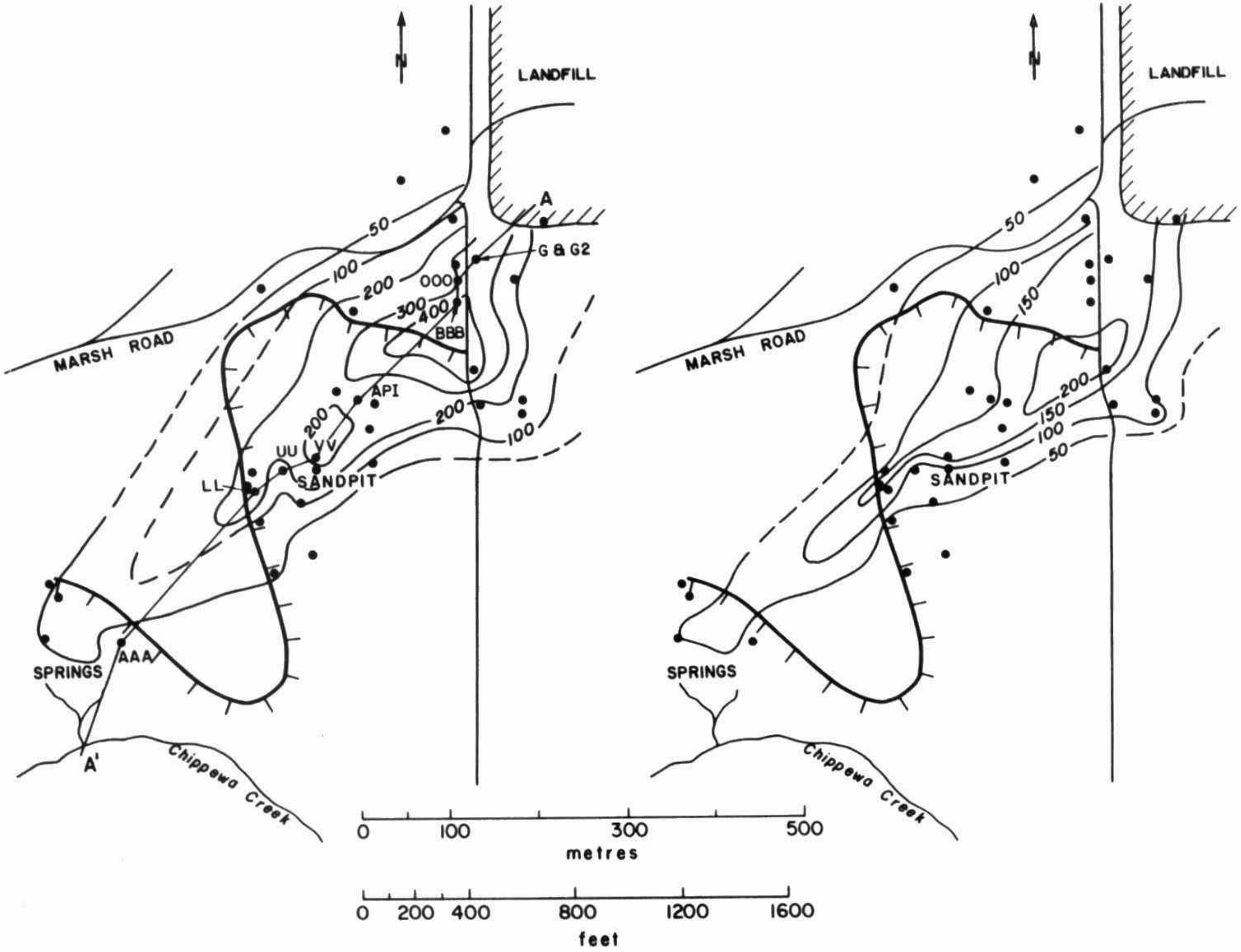


Figure 3. Plane view of the North Bay leachate plume showing the distribution of the maximum chloride (left) and TOC (right) concentrations Data from 1984.

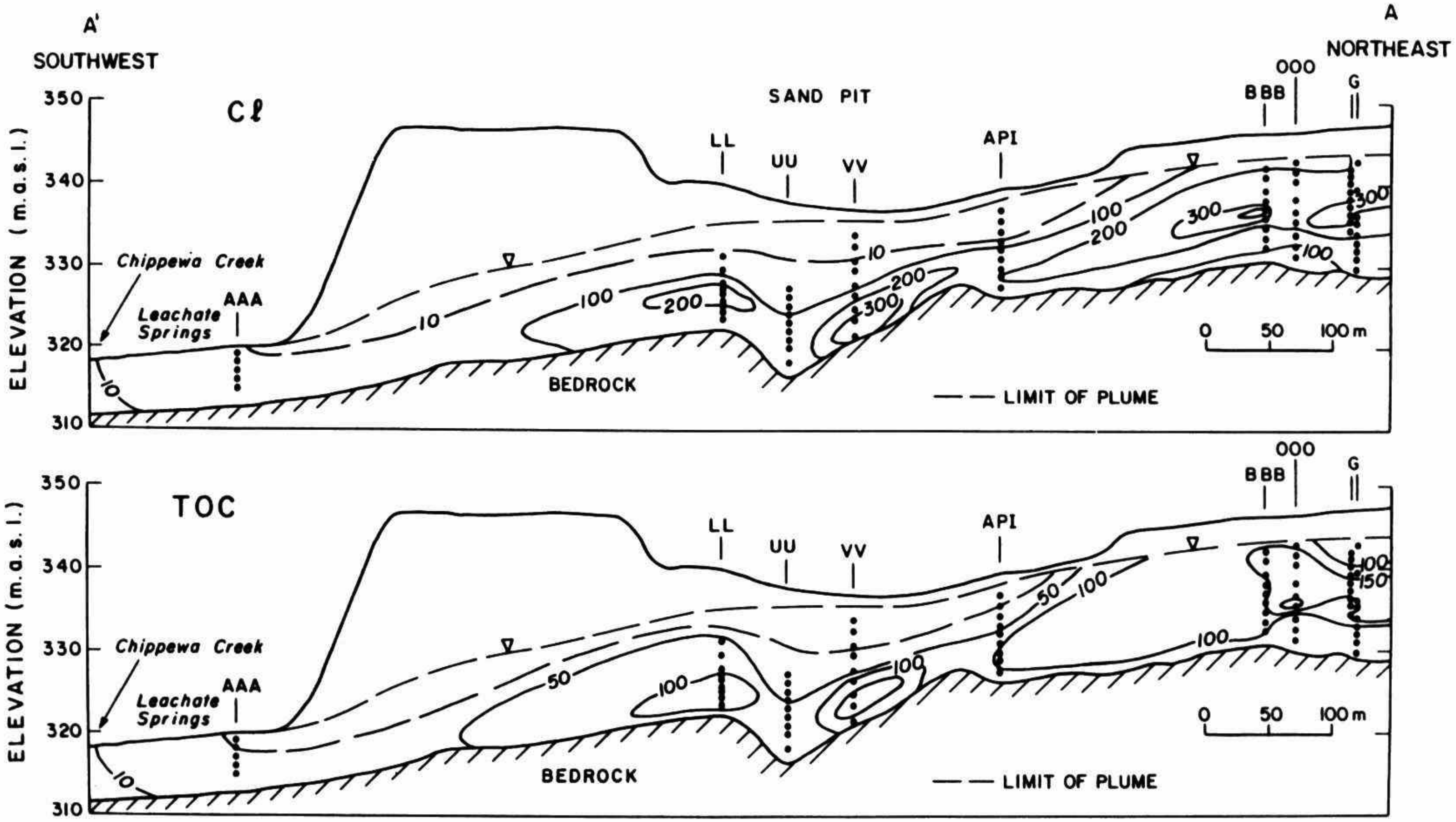


Figure 4. Distribution of chloride and TOC in groundwater samples along cross-section AA' (see Figure 3). Data from 1984.

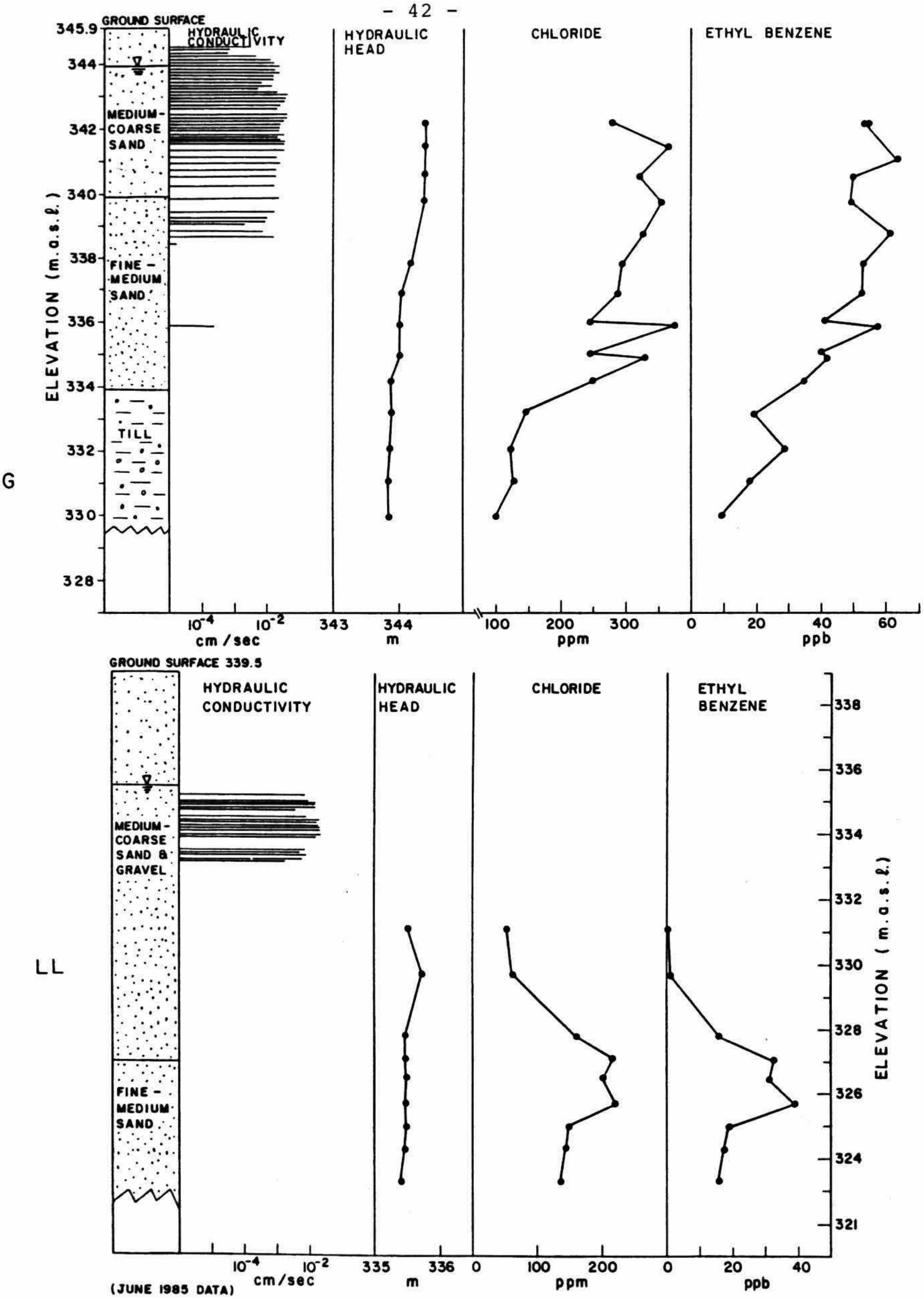


Figure 5. Vertical variation of selected hydraulic and geochemical parameters at locations G and LL (see Figure 3) in the North Bay leachate plume.

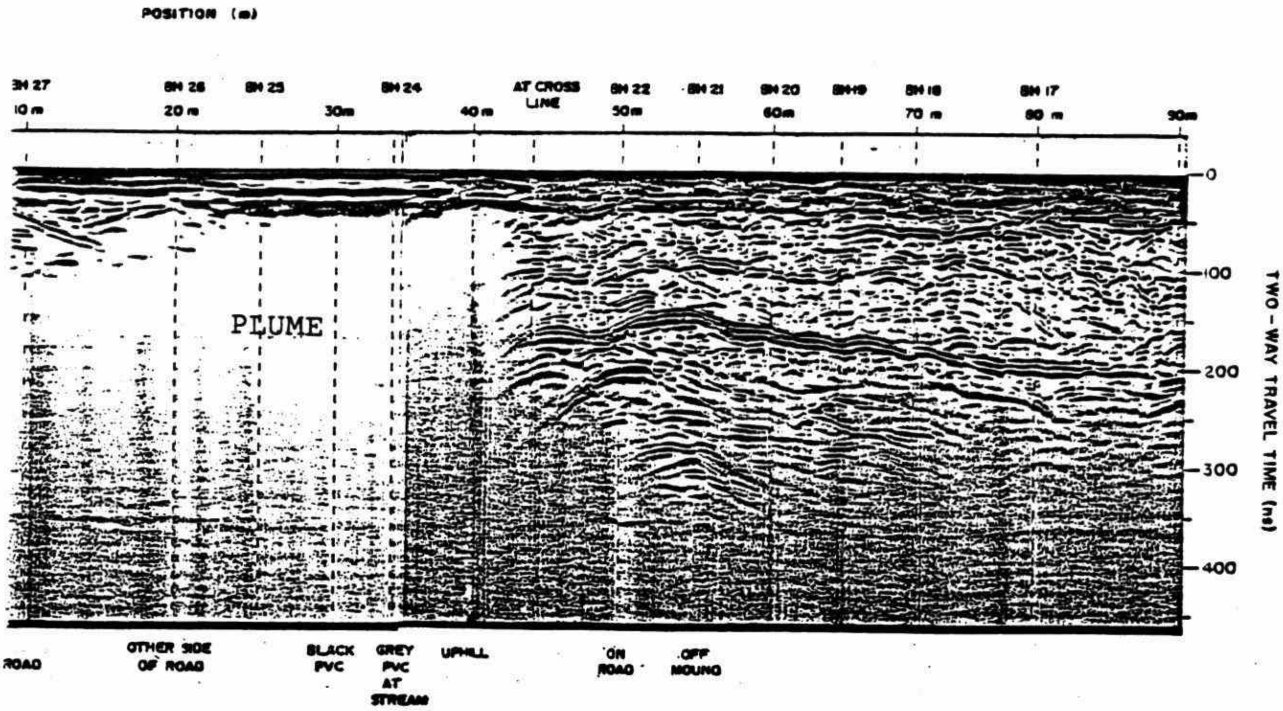
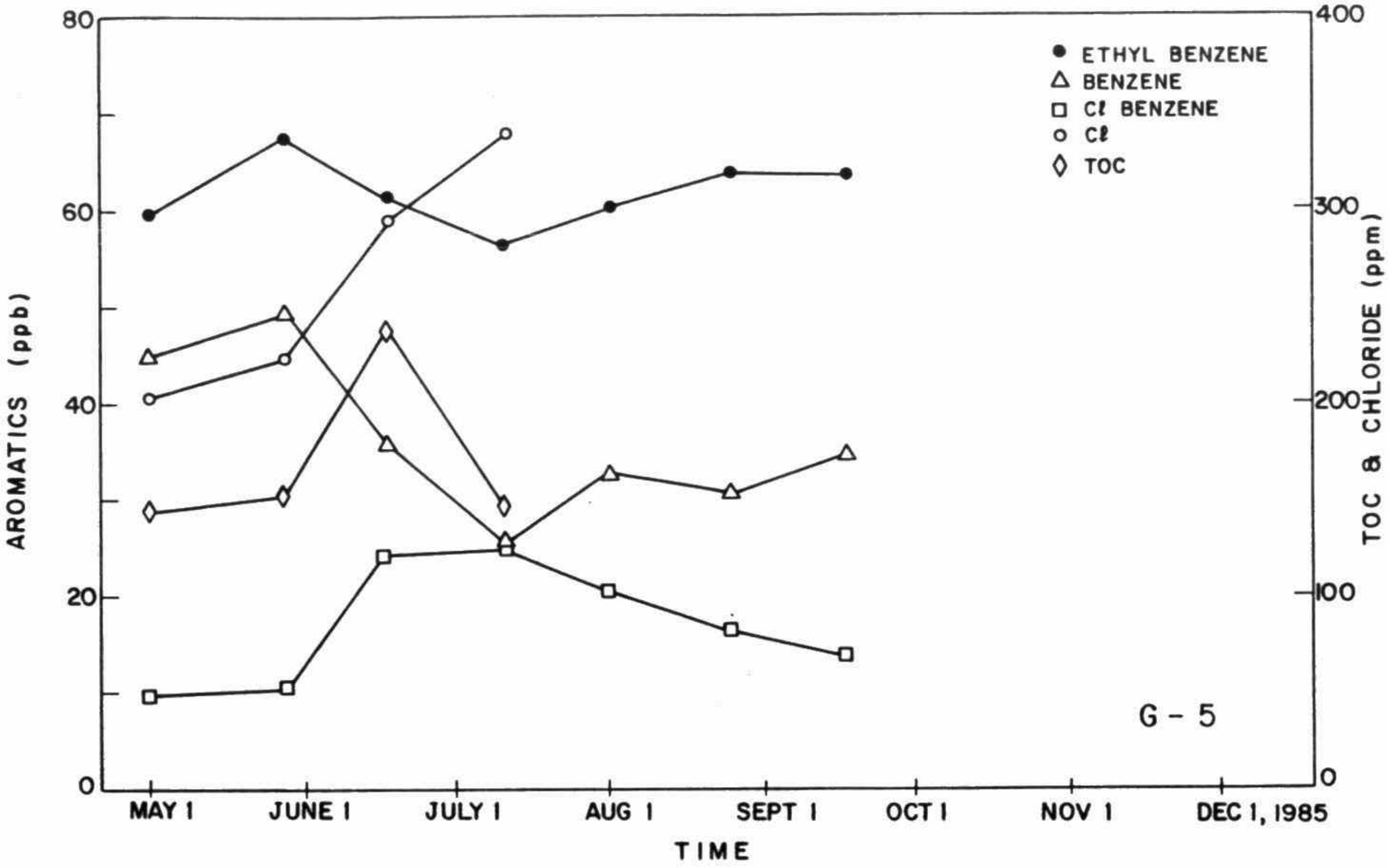


Figure 6. Ground Penetrating Radar profile at the North Bay site near API (see Figure 3) showing the detailed stratigraphy of the sands (right) being masked by the leachate plume (left).



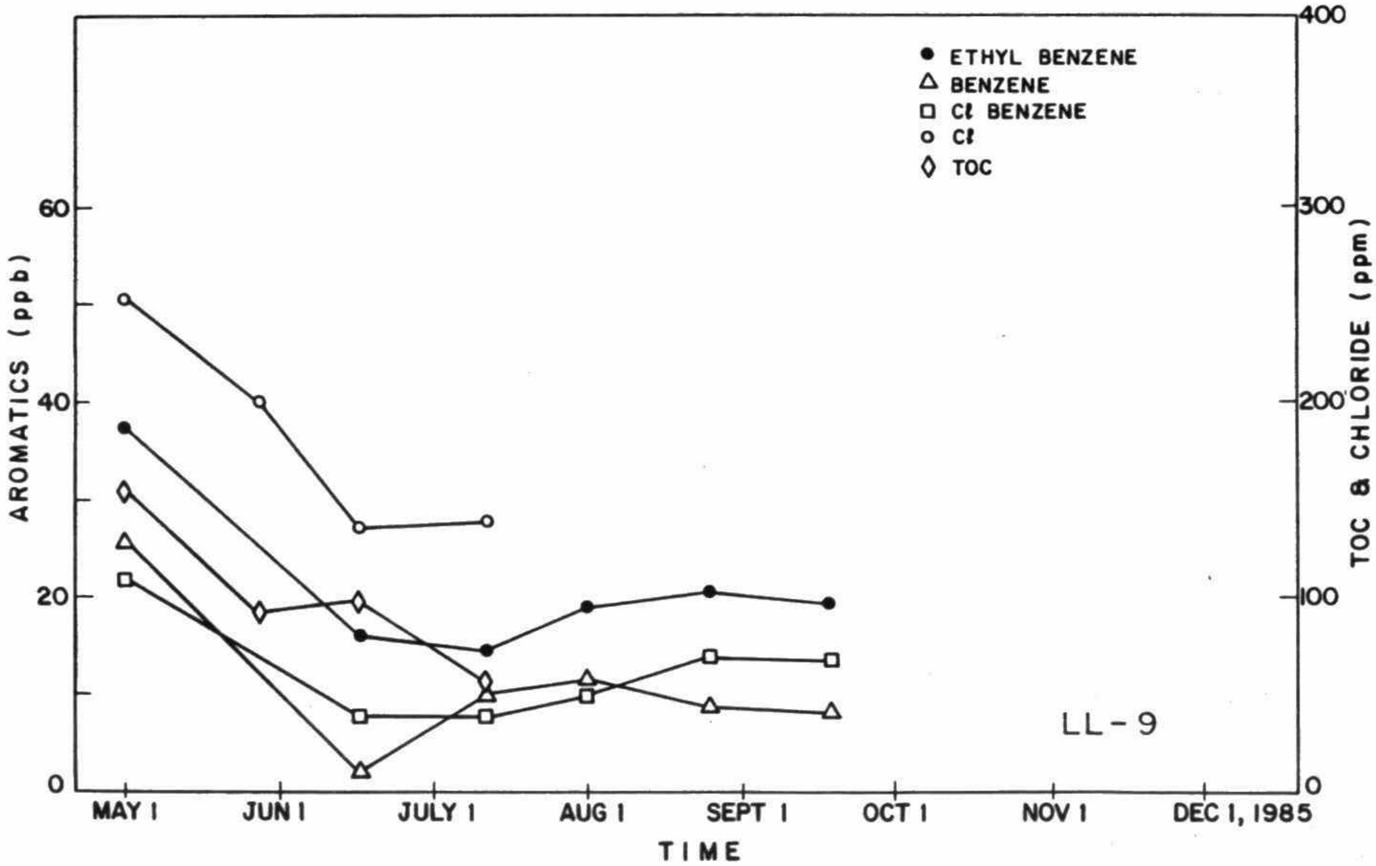


Figure 7. Temporal variability of groundwater quality at piezometers G-5 and LL-9, North Bay leachate plume.

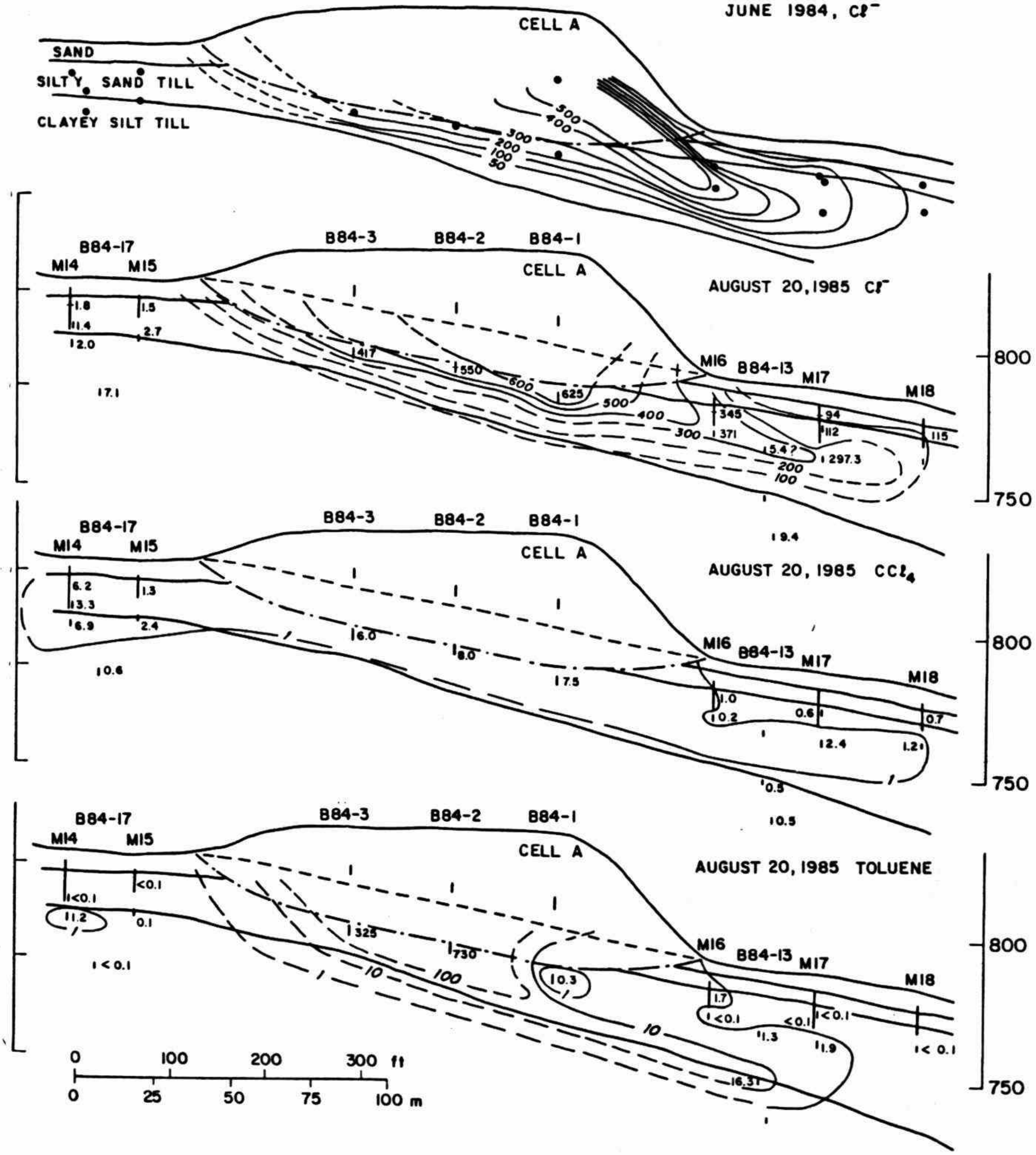


Figure 8. Cross-sections through the oldest landfilled cell at the New Borden site showing the distribution of chloride in 1984 and August 1985; carbon tetrachloride, August 1985; and toluene, August, 1985.

THE ACCURATE DETERMINATION OF IN-SITU CONCENTRATIONS OF VOLATILE HYDROCARBONS IN GROUNDWATERS AT THE GLOUCESTER LANDFILL SITE, OTTAWA, ONTARIO

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Key words: Landfill, Leachate, Groundwater, Volatile Hydrocarbons, Gloucester, Contaminant Distribution.

ABSTRACT

The Gloucester Landfill is located near Ottawa, Canada, on a northeast trending ridge of Quaternary age. The ridge comprises a confined aquifer, overlying bedrock, and an unconfined aquifer separated by a silt unit which is an effective aquitard. Two independent Special Waste plumes have previously been identified at the Gloucester Landfill: the southeastern plume, migrating in the confined aquifer, and the northeastern plume, migrating in the unconfined aquifer. The distribution of volatile organic contaminants at the northeastern plume site was examined employing a new sampling technique which used polypropylene syringes as the collection and storage vessels, and a peristaltic pump to bring the leachate to the surface. Laboratory and field evaluations of this method have shown that the syringes are poor storage containers, and losses ($\approx$10%) of some volatiles occur when sampling takes place through a peristaltic pump. Whether these losses are due to interactions with the tubing, or the suction of the pump bears further investigation.

Groundwater velocity measurements taken across the study area varied considerably ($<$ 1 cm/day to 14 cm/day), indicating that the heterogeneities of the surficial sand unit are an important factor in contaminant migration.

Acetate ion was the only identifiable organic acid anion present in the leachate, and is measurable only in areas where the Special Waste contamination is significant. The distribution of volatile organic contaminants and inorganic anions seems to be related principally to the disposal history of the site, and the variable velocity of the groundwater. Sorption interactions are not well described by existing models, possibly because the organic content of the sediment is low ($<$ 0.1%).

THE DISTRIBUTION OF VOLATILE ORGANIC CONTAMINANTS IN A LEACHATE PLUME, GLOUCESTER, ONTARIO

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INTRODUCTION

In 1957, Transport Canada leased six hectares of land south of Ottawa from the then township of Gloucester to be used as a domestic waste disposal site (Figure 1). Between 1969 and 1980 various federal agencies disposed of "special" waste chemicals within a designated area, the Special Waste Compound, at the landfill. A "special" waste is one which requires particular care in handling and disposal because of its toxicity to humans and other organisms in the environment (A.J. Graham Engineering Consultants Ltd., 1985). Pollutants that may have been generated by the federal agencies which used the Gloucester disposal site include organic solvents, pesticides, inorganic acids and bases, and hazardous salts of mercury (Jackson _et al._, 1985).

In 1977, Gartner Lee Associates undertook a reconnaissance survey of the Gloucester Landfill. This study indicated that leachate had travelled a considerable distance from the disposal area and toward a small industrial park relying on wells for its water supply. Subsequent and more detailed work undertaken by Gartner Lee Associaltes in 1978, showed that at least two independant plumes of contaminated groundwater were migrating off the landfill site.

Insufficient data were collected in 1978 to properly define the extent of the plumes.

In 1979, the National Hydrology Research Institute (N.H.R.I.) of Environment Canada began a study of ground water contamination at the Gloucester Landfill, focussing on the plume in the southeast portion of the site (here after referred to as the southeast plume) (Jackson _et al._, 1985).

The Gloucester landfill is located on marine and littoral sands overlying a silt aquitard which, in turn, overlies a second, confined, aquifer composed of poorly sorted glacial outwash sediments. Detailed mapping of the extent of the volatile organic plumes revealed that some of the contamination infiltrated the confined aquifer and has been transported a considerable distance from the Special Waste Compound.

This project was initiated, in 1984, with the objectives: (1) to use and evaluate a new sampling technique for the determination of volatile organic compounds in water; (2) to determine the extent of the contamination and the distribution of the volatile organics in the contaminant plume located in the northeast portion of the landfill (here after referred to as the northeast plume).

EXPERIMENTAL

Sampling

Samples were collected at 22 multilevel installations (Figure 2). Multilevels were constructed using P.V.C. central stocks each supporting 5-6 6.3 mm diameter polyethylene tubes which extend from the ground surface to the bottom of the unconfined aquifer (7 m depth). The buried ends of the polyethylene tubes are wrapped in 105 um nytex mesh. No glue was used in the construction of the multilevel samplers; parts were either pressed together or held in place with plastic clips (Figure 3).

Samples were collected (and stored) in polypropylene syringes using a volatile organic sampler developed by Farrington Lockwood Co. Ltd. (Farrington Lockwood, 1983) (Figure 4). The system permits collection and analysis of samples without exposure to the atmosphere. All parts of the sampling equipment that come into direct contact with the water being sampled were transported to and from the field in sealed plastic bags in a tightly sealed cooler; this measure prevented exposure to, and contamination from, gasoline fumes. The Volatile Organic Sampler (V.O.S.) was connected after a Masterflex peristaltic pump and 10 minutes of pumping was carried out prior to collecting a sample for analysis to insure that representative ground water was obtained.

The collection and analysis of 7 field blanks (organic free deionized water) has indicated that the cross contamination of samples from the silicone tubing in the peristaltic pump is not a problem.

Analytical Methods

Within 24 hours of collection, samples were analysed for anions, total alkalinity and volatile organic contaminants. Anion analysis was carried out using a Dionex System 12

Analyser with and autosampler, an anion concentrator column (#030986) an anion separator column (#030985) and a hollow filter suppressor unit (#035691). The precision of the analytical method is estimated to be +/-5% for the determination of chloride ion, sulfate ion and acetate ion. The accuracy of the analyses was checked by including laboratory standards constituting a complete calibration set in each analytical batch.

The analysis of selected leachate samples for weak organic acids was carried out using the Ion Chromatography Exclusion Mode (I.C.E.) in which the System 12 Analyser is equipped with a cation trap (#030975), a separator column (#030890) and a supressor column (#030891). These analyses indicated that, of the volatile fatty acids, only acetate is present at measurable concentrations in the ground water at the northeast plume site.

Total alkalinity values were determined using a Metrohm Heriseau E536 Potentiograph, an E535 Dosimat (autotitrator) and an E694 magnetic stirrer. Ground water samples were titrated with a 0.02N HCl solution which was standardised daily against a freshly prepared 0.0236M solution of Na2C03. The analytical precision for this method is estimated to be +/-5%.

Volatile organic compounds were analysed using a Spectrophysics Model 7100 gas chromatograph equipped with an Envirochem Unicon 810 purge and trap unit. Samples (15 mL) were purged 12 minutes with high purity He gas ; a 30 m, 0.25 mm diameter wall coated open tunnel capillary column was used to achieve separation of the compounds, which were then detected with F.I.D. and Hall detectors. The precision of organic analyses was assessed by the analysis of replicate samples (samples collected separately from the same location). Analytical time restrictions made the analysis of duplicate samples (samples split in the laboratory and analysed twice) impossible, i.e., samples had to be analysed within 24 hours of collection; the analysis of duplicates would have caused the storage time of some samples to exceed this restriction. Examination of the replicates collected on the same day suggests a precision of about +/-10% (Table 1). The only samples exceeding these limits were those with contaminant concentrations at or near the detection limit (~1ppb).

Replicates collected up to 10 days apart showed a much greater variability (>50%) which is also evident in replicates collected 1-3 months apart (Table 2). These changes appear to reflect changing groundwater chemistry.

Attempts were made to check the accuracy of the results by analysing a standard solution containing 20 volatile organic compounds in concentrations ranging from 50-200 ug/mL. The standard was prepared by injecting neat 50 uL aliquots of the organic compounds of interest through a teflon septum into a preweighed glass vial filled with H.P.L.C. grade methanol (~30 mL). A 5 mL aliquot of this solution was then injected, through a teflon septum, into a preweighed tedlar bag filled with organic-free deionized water (~2 L). Head space throughout this operation was kept at a minimum to avoid losses of the volatiles into the vapour phase. All glassware, teflon and tedlar were precleaned by rinsing several times with organic-free deionized water and baking several hours at 100°C.

RESULTS AND DISCUSSION

Inorganic Groundwater Geochemistry

Chloride concentration in water sampled from the unconfined aquifer ranges from 1 ug/mL (background) to 157 ug/mL in the more contaminated locations (Figure 5). The highest chloride concentrations appear to be emanating from a source north and west of the study area. In section, the chloride contamination appears to be migrating along the bottom of the unconfined aquifer. High chloride concentrations (40 ug/mL) are present in ground water east of multilevel sampling station 118M (the most easterly located multilevel), thus the extent of the chloride plume has not been firmly defined. However, the location of the plume front has been estimated based on the concentration contour intervals and the definition for the front of a plume given by Jackson _et_ _al._ (1985):

$$Ci = 0.1 \times Cmax \qquad (1)$$

where,

Ci = the concentration of contaminant "i" at the front of the plume
Cmax = the maximum measured concentration of contaminant "i" in the plume

Alkalinity values in the unconfined aquifer range from 0.5 meq/L to 23 meq/L with the lowest values measured at shallow elevations and the higher values measured in deeper ground water (Figure 6). In section, three zones can be defined on the basis of alkalinity: (1) a leached zone located near surface, in which little or no carbonate is present in the sediment (alkalinity <3 meq/L); (2) an intermediate zone (alkalinity 6-10 meq/L) extending from 3-5 m in depth, in which carbonate appears to be the primary contributor to the alkalinity and (3) a high alkalinity zone, located near the bottom of the unconfined aquifer, in which the acetate ion appears to be the dominant contributor.

Acetate concentrations across the site range from <5 mg/L to >1000 mg/L; the highest measured concentrations occur near multilevels 112M and 113M. The front of the acetate plume extends east beyond 118M; its position has been estimated using the same method applied to the chloride plume. In section, it appears that the acetate is migrating along the bottom of the unconfined aquifer.

Sulfate concentrations range from <5 mg/L to 225mg/L at the study area; background levels are <40 mg/L (Figure 8). Sulfate is most concentrated at the northern edge of the study area and, in section, is present throughout the unconfined aquifer.

A narrow zone of low sulfate concentration extending eastward from 20M to 112M (and coinciding with the position of maximum concentrations of acetate and some volatile organics) may be a reflection of sulfate reduction:

$$SO4^{=} + 8e- + 9H+ \rightleftarrows HS^{-} + 4H2O \ ; \quad pe(W) = -3.75 \qquad (2)$$

The extent to which sulfate and bisulfide are related by equation (2) was investigated by Elliot (1985) who observed a positive correlation between ground water pH and bisulfide concentration, as predicted. However, no correlation could be found between the concentrations of sulfate and total sulfide, possibly because the precipitation of heavy metal sulfides acts as a sink for reduced sulfur:

$$Fe^{2+} + 2SO4^{=} + 16H^{+} + 14e- \rightleftarrows FeS_2 + 8H2O \qquad (3)$$

Sulfide concentrations at the site range from <5 ug/L to >100 ug/L; the highest concentrations occur primarily along the bottom of the unconfined aquifer and at the northern edge of the study area.

An intensive redox survey of the site was undertaken by Elliot (1985), who conducted EH measurements, carried out with a Pt electrode, and calculated pe values, on the basis of sulfate ion and total sulfide concentrations. The most reducing conditions are reported to exist between 20M and 112M and east of 114M, along the bottom of the unconfined aquifer (EH=50 mv, pe<-4.6). The reducing environment to the east of 114M may be explained in terms of the normal processes of a closed oxidant system, in which conditions become increasingly reducing with increased distance from the recharge zone (Champ *et al.*, 1979). The low EH and pe values found between 20M and 112M appear to coincide with the positions of the maximum measured concentrations of several organic contaminants, suggesting that these contaminants are involved in redox processes responsible for the reducing environment.

Volatile Organic Contamination

Twenty volatile organic compounds have been identified in the ground water at the northeast plume site by G.C./M.S. (Zenon Environmental, 1985). Of these, 1,2 dichloroethane (1,2 DCEA), benzene, trichloroethene (TCEY), toluene, chlorobenzene (Cl-BENZ), and ethyl benzene (Et-BENZ) have been studied quantitatively. Tetrahydrofuran (THF) and diethyl ether (DEE) have been tentatively identified by G.C. and also studied quantitatively, but their presence has not been confirmed by M.S. (Figures 9-15)..

The distribution of volatile organic contaminants in plan view suggests that the source is located west of the study area. The plumes appear to be migrating along a very narrow path between 99PM and 100PM (25 m wide) which extends east beyond 118M. However, the lack of lateral control east of 112M restricts a firm definition of the plume width to the western and central portions of the study area. Toluene, Cl-BENZ, 1,2 DCEA, THF, and benzene all show two concentration maxima: a well defined maximum between 109M and 113M, and a poorly defined maximum beginning near 118M and extending east. In section, the contaminants appear to be following two flow paths: in the western portion of the study area, toluene and Et-BENZ occur at depths of about 4-5 m while the remaining chemicals are most concentrated at depths of 6-7 m. East of 109M, all volatiles except DEE appear to be migrating at about 5 m depth. This pattern continues until between 115M and 117M where the concentration maxima are once again found at the bottom of the unconfined aquifer.

Discussion

Water sampled at the northeast plume site and analysed at the University of Waterloo contained significant levels of methane indicating that methane fermentation is occurring in the leachate. Acetate concentrations in the northern section of the study area, corresponding to the oldest disposal operations, were found to be below the analytical detection limit, whereas concentrations exceed 1000 mg/L at piezometers located in the volatile organic plume. Since acetate is known to be rapidly consumed under both aerobic and anaerobic conditions (McCarty et al., 1984; Hoeks and Borst, 1982) these data suggest that biological activity may be inhibited by the presence of the special wastes in the leachate.

The distribution of chloride ion at the northeast plume site suggests that its source lies north and west of the study area, and that the plume itself is migrating in a south easterly direction. However, this interpretation is inconsistant with the flow lines predicted from water table elevation data and with the apparent flow direction of the acetate ion and the volatile organic contaminants (east). An explanation for this seeming contradiction is possible if two assumptions are made: (1) the chloride ion emanates from a line source (not a point source) (2) ground water velocity varies across the site. The first assumption is justified because the disposal of municipal wastes is known to have occurred throughout the area west of the railway tracks from Leitrim Road to the north , to Delzotto Road to the south.

Air photos of the area show that the northern disposal operations were completed more than ten years prior to the completion of the more southerly operations. The second assumption also seems justified on the basis of ground water velocities measured directly, using a point dilution device (Belanger, 1984), and those calculated from hydraulic conductivity and water table gradient data (velocities range from <1 to 14 cm/day). A conceptual model, which ignores the effects of dispersion, sorption, and transformations, and which assumes a three year continuous source of contamination in a variable ground water velocity domain (Figure 16a) shows a resultant plume which is oriented at an acute angle to the actual flow direction. The situation at the northeast plume site may be more closely simulated by introducing additional contaminant sources ten years after the initial dumping (Figure 16b) (These sources are also assumed to be continuous for three years). The relationships evident in this simple model appear to closely resemble the field relationships between chloride and the volatile organic contaminants at the northeast plume site. The orientation of the chloride plume has been extensively mapped by L.E. Stephens (Geological Survey of Canada, 1985, pers. com.) using electromagnetic methods (Stephens and Graham, 1985) (Figure 17). It can be seen from this work that north of the study area the chloride plume extends much further east than in the southern portion of the study area. This distribution probably reflects the relative ages of the disposal operations.

The lateral distributions of toluene, benzene, Cl-BENZ, 1,2 DCEA, and DEE suggest that more than one dumping of these chemicals has occurred. The high concentrations east of 117M appear to be the result of an early dumping, while the concentration maxima further west are the result of more recent disposals. The distribution patterns of volatile organic contaminants could be partly the result of sorptive interactions with the aquifer material. To investigate this possibility, the retardation factors for the various contaminants were estimated using the equation:

$$(Rf - 1) = (Xi/Tref - Xi) \tag{4}$$

where,

$$Xi = Tref - Ti \tag{5}$$

Tref = the length of the plume of a conservative contaminant

Ti = the length of contaminant plume "i"

Since the location of the source is unknown, Tref and Ti cannot be measured directly. An estimate of the length of the chloride plume (Tref) can be calculated from ground water velocity measurements and the approximate age of the disposal site (12 years). Unfortunately, chloride cannot be used as the reference plume in this study because the contaminant concentration maxima most clearly defined by the field data appear to correspond to at least the second of a series of disposals; it cannot be assumed that the chloride and the volatile organic contaminants were introduced to the aquifer at the same time. Nevertheless, the length of the chloride plume can be used to determine the length of an alternate reference plume, using equation (5).

The position of the acetate plume suggests that its source may have been the same as that of the volatile organics. The high solubility of acetate in water permits it to migrate at approximately the same velocity as the ground water. The apparently low biological activity in the organic plume eleminates the primary cause of acetate attenuation. Thus, acetate ion has been used as the reference in determining the retardation factors of the various volatile organics. The quantity "Xi" is measured as the distance between the front of the acetate plume and the front of contaminant plume "i". The retardation factors of the volatiles have been calculated using equation (4), and log(Rf-1) has been plotted against logKow according to the following equation derived by Patterson et al. (1985) for volatile contaminants migrating in the confined aquifer at the southeast plume site:

$$\log(Rf - 1) = 0.05 \log Kow - 0.065; \quad (r = 0.098) \qquad (6)$$

where,

Rf = the retardation factor of a given volatile organic contaminant

Kow = the octanol/water partition coefficient for the same contaminant

The resulting graph shows a positive correlation between the two parameters, but considerably more scatter is evident in these data points than in those of Patterson et al. (1985) (Table 3, Figure 18, equation (7)).

$$\log(Rf - 1) = 0.09 \log Kow - 0.718; \quad (r = 0.66) \qquad (7)$$

The high scatter evident in the northeast plume data could be a reflection of the fact that the plume lengths are only slightly greater than the length of the potential disposal area from which the contaminants originated. Thus, the exact location of the disposals may have varied as well as the timing. The relative importance of these parameters was investigated using a two dimensional solution to the advection/dispersion equation, which assumes a point source and a non transformable contaminant (Baestle, 1969):

$$C_i = \frac{M_i}{4\sqrt{D_x D_y}\,\frac{t}{Rf}}\, e^{-\left\{\frac{D_y X^2 + Y^2 D_x}{4 D_x D_y \frac{t}{Rf}}\right\}} \qquad (8)$$

where,

Ci = the concentration of contaminant "i" (M/L)
Mi = the amount of contaminant "i" initially dumped (M)
Dx = dispersion coefficient in the x direction (L /T)
Dy = dispersion coefficient in the y direction (L /T)
t = time (T)
X = x + Vxt/Rf
x = distance in the x direction (L)
Vx = ground water velocity in the x direction (L/T)
y = distance from the source in the y direction (L)

If both acetate and chloride are conservative contaminants and they were codisposed, then the two plumes should exactly coincide in position. However, at the northeast plume site, chloride has migrated an estimated 30 m further east than acetate. This relationship implies that either the contaminant sources are located 30 m apart (the disposals were simultaneous) or the acetate was initially dumped three years after chloride (assuming chloride was dumped 12 years before sampling; the age of the disposal site). These estimated uncertainties in the timing and location of disposal may be applied to the calculation of retardation factors of volatile organics relative to acetate. The following scenerios bracket the widest possible range of retardation factors, calculated using equation (8), which can reasonably be expected (i.e. volatile organics have Rf>1):

(1) Acetate and volatile organics were codisposed 9 years before sampling (same location).

(2) Acetate and volatile organics were codisposed 12 years before sampling (same location).

(3) Acetate and volatile organics were disposed 12 years before sampling and 30 m apart (acetate disposed furthest west). This assumption implies the same retardation factors as the assumption that acetate and the volatile organics were disposed in the same location but three years apart (volatiles disposed 12 years before sampling, acetate disposed 9 years before sampling).

(4) Acetate and volatile organics were disposed 9 years before sampling and 30 m apart (volatiles disposed furthest west). This assumption implies the same retardation factors as the assumption that acetate and the volatile organics were disposed in the same location but three years apart (volatiles disposed 9 years before sampling, acetate disposed 12 years before sampling).

Best fit Rf values have been determined for each of the above scenerios using equation (8). The results are compared with Rf values determined from equations (4) and (5) (which assume acetate and volatiles were codisposed 9 years before sampling) and are listed in Table 4.

Since there is evidence that more than one dumping has taken place, and that acetate appears to be associated with a later dumping, the first scenerio seems to be the most likely one. However, the above analysis does not clearly support any of the scenerios considered; the Rf values are all very similar. Jackson et al. (1985) have shown, using the work of Schwarzenbach and Westall (1981), that Rf values close to 1.0

may be expected in systems where the aquifer sediment contains a low fraction of organic carbon (Figure 19).

Equations (6) and (7) may be expanded as follows:

$$\log(Rf - 1) = a\log Kow + \log foc + \log[Pb/n] + b \quad (9)$$

where,

a, b = constants
foc = the weight fraction of organic carbon in the aquifer sediment (dimensionless)
Pb = the bulk density of the aquifer sediment (M/L
n = the porosity (dimensionless)

According to Schwarzenbach and Westall (1981,1985), the constants "a", and "b" depend on the class of compounds being sorbed and on the properties of the sorbent (sediment). Since the same compounds have been studied in both contaminant plumes at the Gloucester Landfill, the differences between the regression parameters "a" and "b" for the two lines in Figure 18 (northeast and southeast plumes) must be attributable to differences in sediment at the two plume sites. The lipophilicity constant, "a", has been reported to vary between 0.50 and 0.87 for natural sorbents including aquifer material and lake sediment (Schwarzenbach and Westall, 1981). In general, "a" decreases in value as the weight fraction of organic carbon in the sorbent decreases; silica ($foc<0.0001$) showed a lipophilicity constant of 0.12. Thus, the low value of "a" in equation (7) may reflect a low fraction of organic carbon in the sediment comprising the unconfined aquifer.

A calculated fraction of organic carbon for the northeast plume site can be determined assuming that the values of "b", Pb, and n are the same as those at the southeast plume site.

By combining equations (6), (7) and (9) it can be shown that:

$$\log f_{oc} \text{ "n.e."} = -0.718 + 0.065 + \log f_{oc} \text{ "s.e."} \qquad (10)$$

from which,

$$\log f_{oc} \text{ "n.e."} = 0.0007$$

where,

foc "n.e." = the fraction of organic carbon in the sediment at the northeast plume site

foc "s.e." = the fraction of organic carbon in the sediment at the southeast plume site (0.0031)

This calculated fraction of organic carbon compares well with independant measurements of the foc carried out by the University of Waterloo, which range from 0.0003 to 0.001.

CONCLUSIONS

The velocity at which a volatile organic contaminant will travel in ground water appears to be very dependant on the organic carbon content of the aquifer sediment. At the northeast plume site, where the fraction of organic carbon in the sediment is low (0.0003-0.001), the retardation factors for DEE, THF, 1.2 DCEA, BENZENE, TOLUENE, and Cl-BENZ have a maximum range of 1.1 - 1.8. At the southeast plume site, where in the confined aquifer the fraction of organic carbon is 0.0031, the range in retardation factors is from 2.2 - 8.8 for DEE, THF, 1,2 DCEA, and BENZENE (Jackson et al., 1985). These data indicate that in some sediments low in organic carbon, volatile organic chemicals could travel at nearly the same velocity as the ground water.

Ground water velocities measured across the northeast site indicate that structural heterogeneities exist in the unconfined aquifer and may be responsible for the channeling of contaminants, causing narrow plumes which may prove difficult to locate in any but the most detailed drilling programs. Also, this channeling could result in the migration of contaminants at velocities greater than previously expected.

Total bisulfide concentrations measured at piezometers located in the most contaminated portions of the northeast plume are higher than those measured at piezometers in less contaminated locations, suggesting that sulfate reduction is occurring in the most contaminated portions of the plume. This observation, plus the detection of methane in the ground water (samples were collected and analysed for methane by the University of Waterloo) indicates that microbial activity is present in the unconfined aquifer. However, the high concentrations of acetate which appear to persist in the most contaminated portion of the volatile organic plume suggests that the biological activity is inhibited by the special wastes.

The analysis of replicate samples has indicated that significant small scale variations occur in the concentrations of volatile organics in ground water over short periods of time (<10 days). The significance of these variations appears to increase with time. The extent to which the variations result from sampling equipment and storage vessels bears further investigation.

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Table 1: Analysis of replicate samples collected on the same day.

Compound	Port					
	101PM0	107M2	112M1	99PM4	114M1	115M5
DEE	nd, <1	19, 19	546, 561	nd, nd	nd, nd	nd, nd
THF	nd, nd	11, 11	54, 58	nd, nd	nd, nd	nd, nd
12DCEA	nd, nd	7, 7	3, 3	nd, nd	nd, nd	nd, nd
BENZENE	<1, <1	101, 99	2, 2	nd, nd	nd, nd	nd, nd
TCEY	nd, nd	1, 1	<1, <1	nd, nd	nd, nd	nd, nd
TOLUENE	<1, <1	1, 1	nd, nd	nd, nd	nd, nd	nd, nd
CL-BENZ	nd, nd	2, 2	nd, nd	nd, nd	nd, nd	nd, nd
ET-BENZ	nd, nd	<1, <1	nd, nd	nd, nd	nd, nd	nd, nd

nd = not detected.

Table 2: Analysis of replicates collected 10 days, 1 month and 2 months apart.

Port			Compound			
	DEE	THF	12DCEA	BENZENE	TCEY	TOLUENE
Replicates sampled 10 days apart						
112M1	546,640	54,75	3,4	2,2	nd, nd	nd,<1
2	122,99	26,12	28,23	181,160	2,2	118,107
3	19,19	nd,nd	7,5	84,83	2,3	4,4
4	22,14	nd,nd	2,2	78,73	2,2	2,2
5	3,nd	nd,nd	4,2	31,20	nd,nd	2,2
Replicates sampled 1 month apart						
110M1	572,422	66,45	7,4	3,2	nd,nd	<1,<1
2	63,56	29,6	11,10	135,138	2,2	219,201
Replicates sampled 2 months apart						
106M2	13,27	nd,5	14,20	41,53	158,71	<1,<1
3	<1,5	nd,9	<1,<1	26,13	42,24	<1,<1
5	nd,nd	nd,nd	nd,nd	nd,nd	<1,nd	nd,<1

nd = not detected.

Table 3: Log Kow's and retardation factors for volatile organic contaminants at the northeast and southeast study areas.

Compound	Kow	Northeast study area Rf	Southeast study area Rf
THF	2.88	1.2	2.2
DEE	7.76	1.2	3.3
1,2 DCEA	30.2	1.3	7.6
BENZENE	110	1.2	8.8
TOLUENE	490	1.3	n.r.
Cl-BENZ	692	1.3	n.r.

Kow values taken from Hansch and Leo (1979).
Retardation factors for volatile organic contaminants in the southeast study area were first reported by Patterson et al., (1985).
n.r. = not reported.
The retardation factor for TCEY has not been included in this analysis because the position of the concentration maximum (Figure 12) indicates that it was not codisposed with the other volatiles under study.

Table 4: Retardation factors for volatile organic contaminants detected at the northeast and southeast study areas.

Compound	Rf(1)	Rf(2)	Rf(3)	Rf(4)	Rf(5)	Rf(6)
THF	1.2	1.4	1.6	1.1	1.2	2.2
DEE	1.2	1.4	1.6	1.1	1.2	3.3
12DCEA	1.3	1.5	1.8	1.2	1.2	7.6
BENZENE	1.3	1.5	1.7	1.1	1.2	8.8
TOLUENE	1.4	1.6	1.8	1.2	1.3	n.r.
CL-BENZ	1.4	1.6	1.8	1.2	1.4	n.r.

Rf(i) = best fit retardation factor using equation (8); determined for scenerio "i" (see text), for i = 1-4.

Rf(5) = Retardation factors calculated using equations (4) and (5) for contaminants at the northeast plume site.

Rf(6) = Retardation factors reported by Patterson _et_ _al._ (1985) for contaminants in the southeast plume.

n.r. = not reported

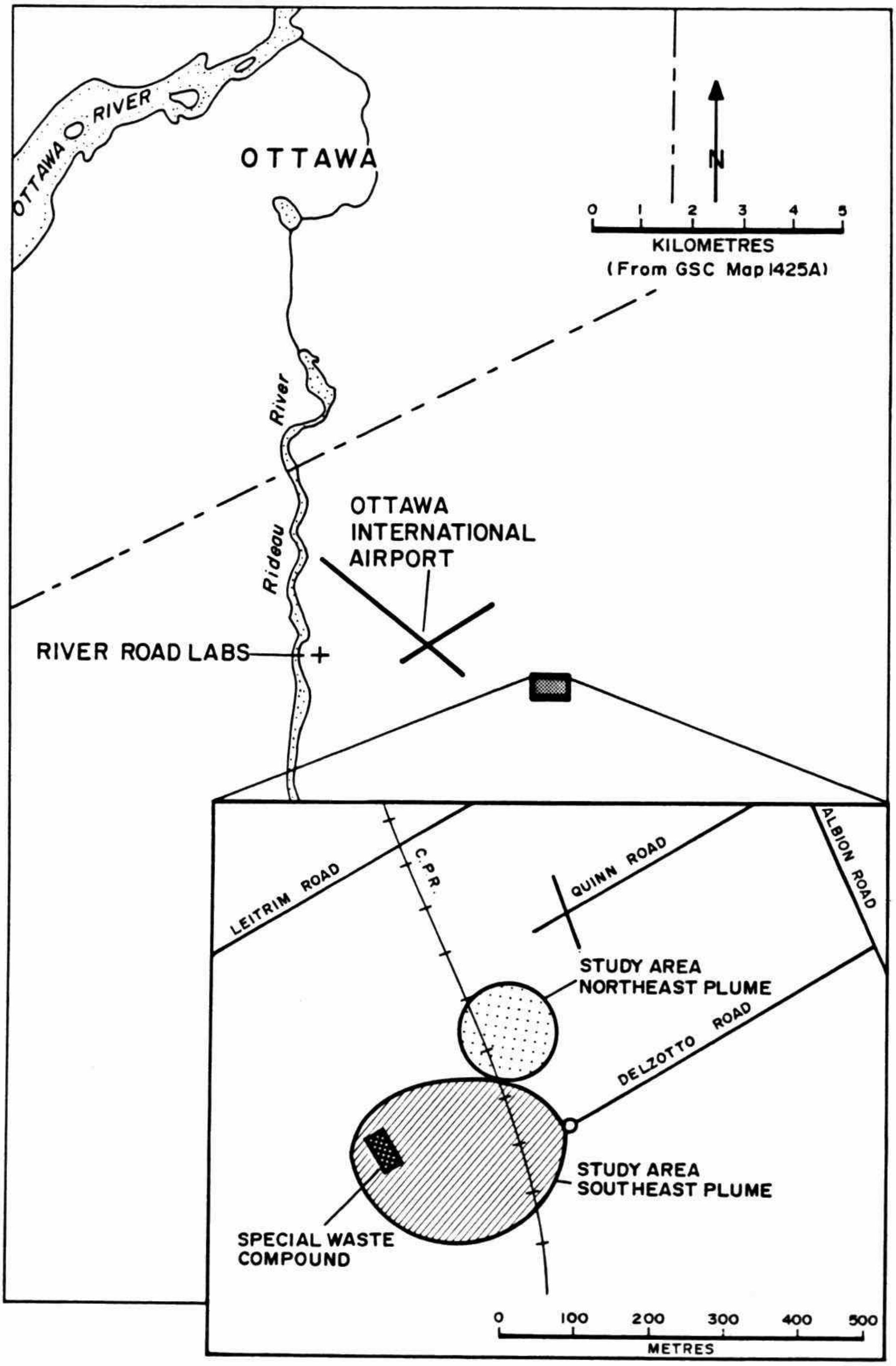


Figure 1: locations of study areas, Gloucester Landfill, near Ottawa, Ontario.

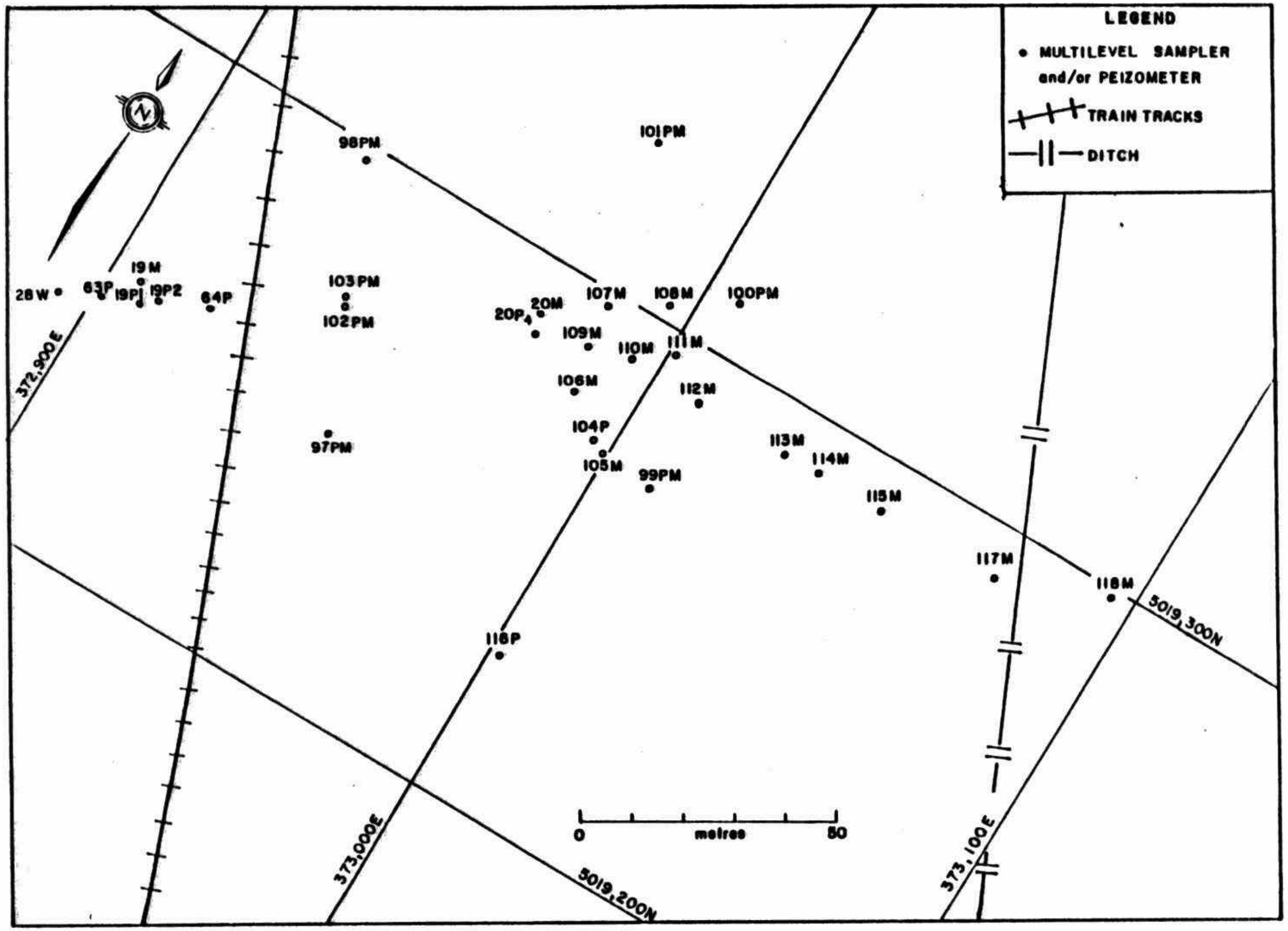


Figure 2: locations of multilevel and piezometer installations at the northeast study area, Gloucester Landfill.

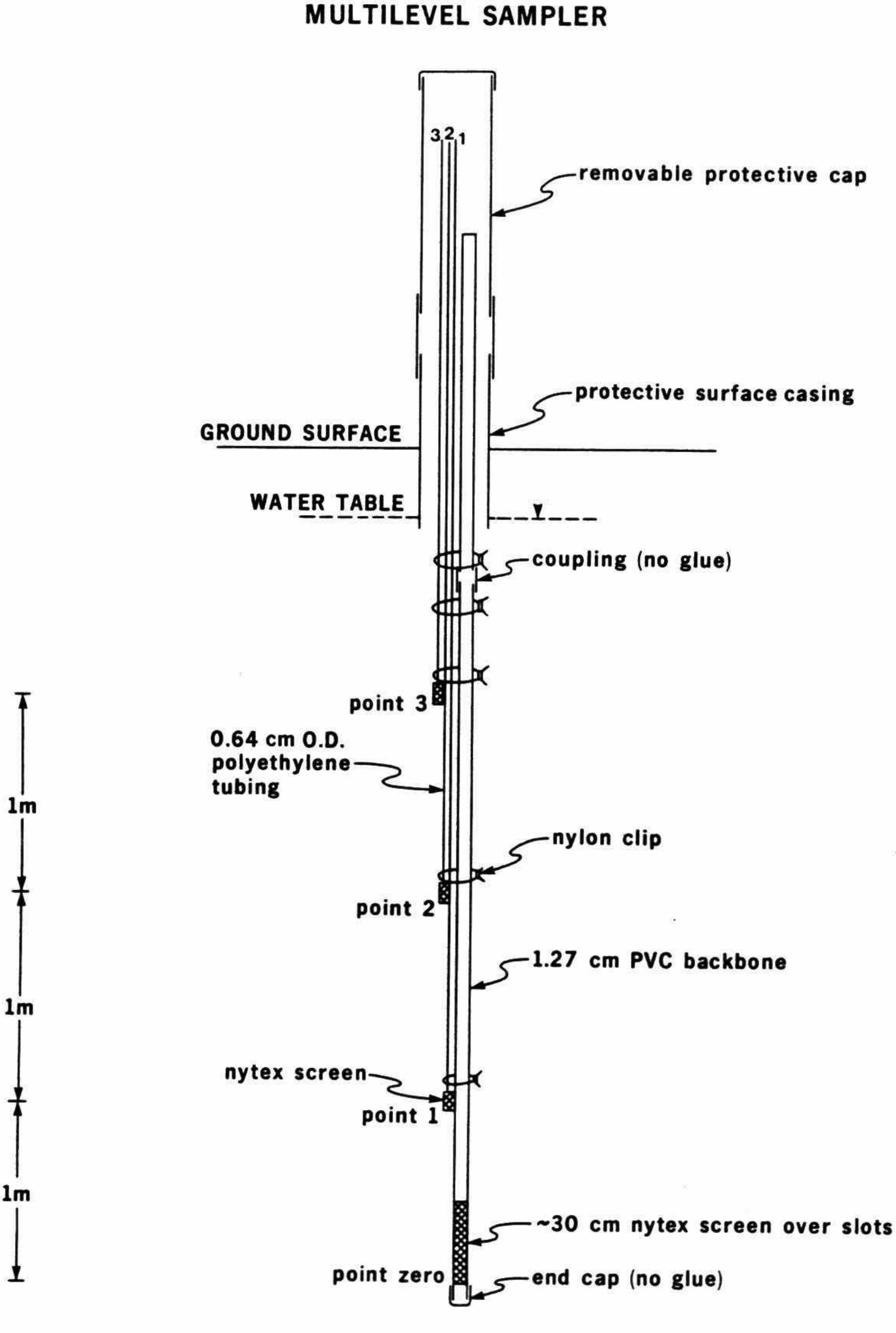


Figure 3: construction of a mulilevel sampler.

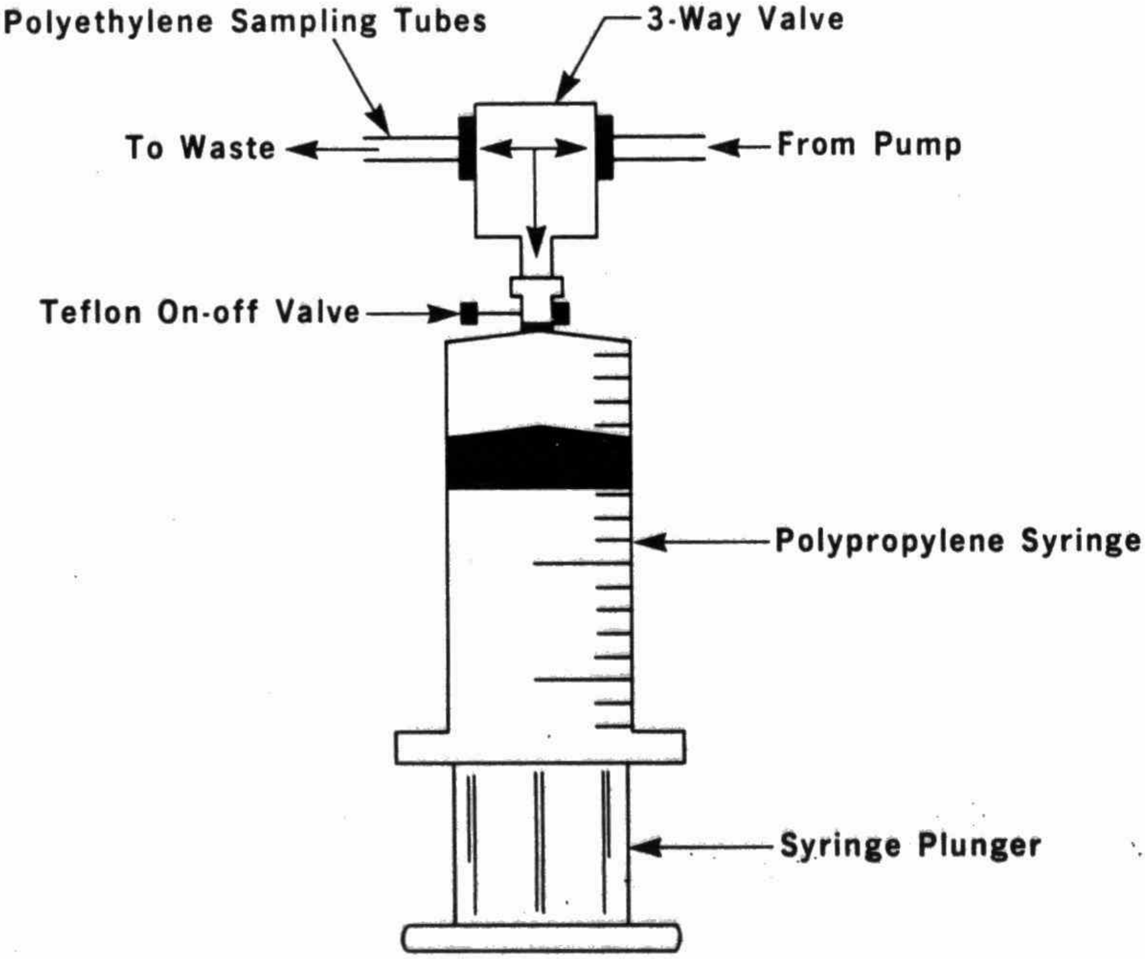


Figure 4: The Volatile Organic Sampler (Farrington Lockwood, 1988).

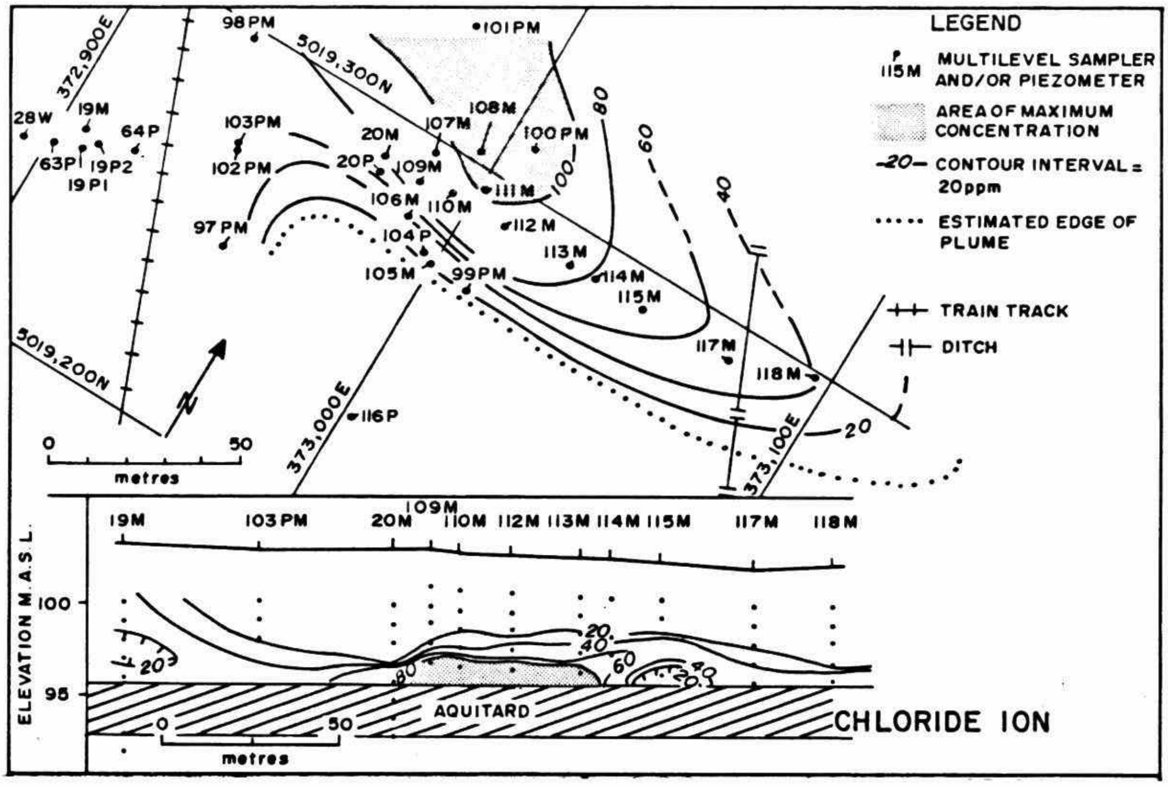
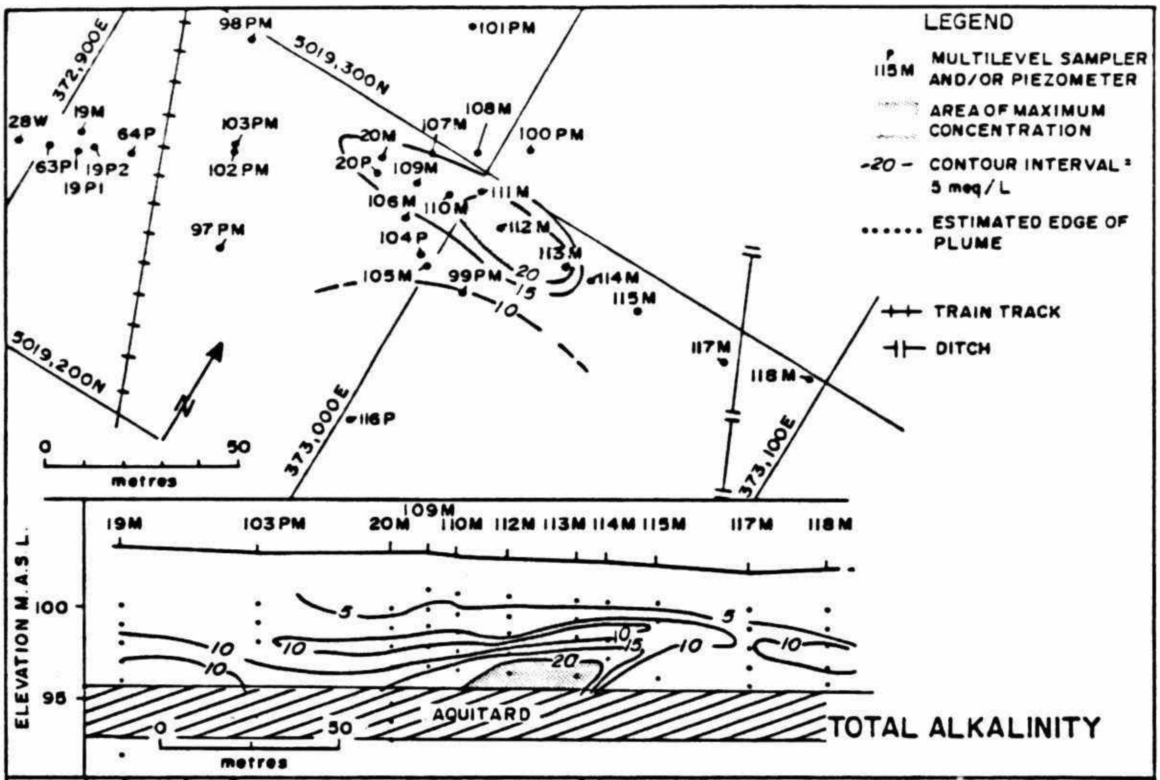


Figure 5: the distribution, in plan and in section, of chloride ion at the northeast study area.



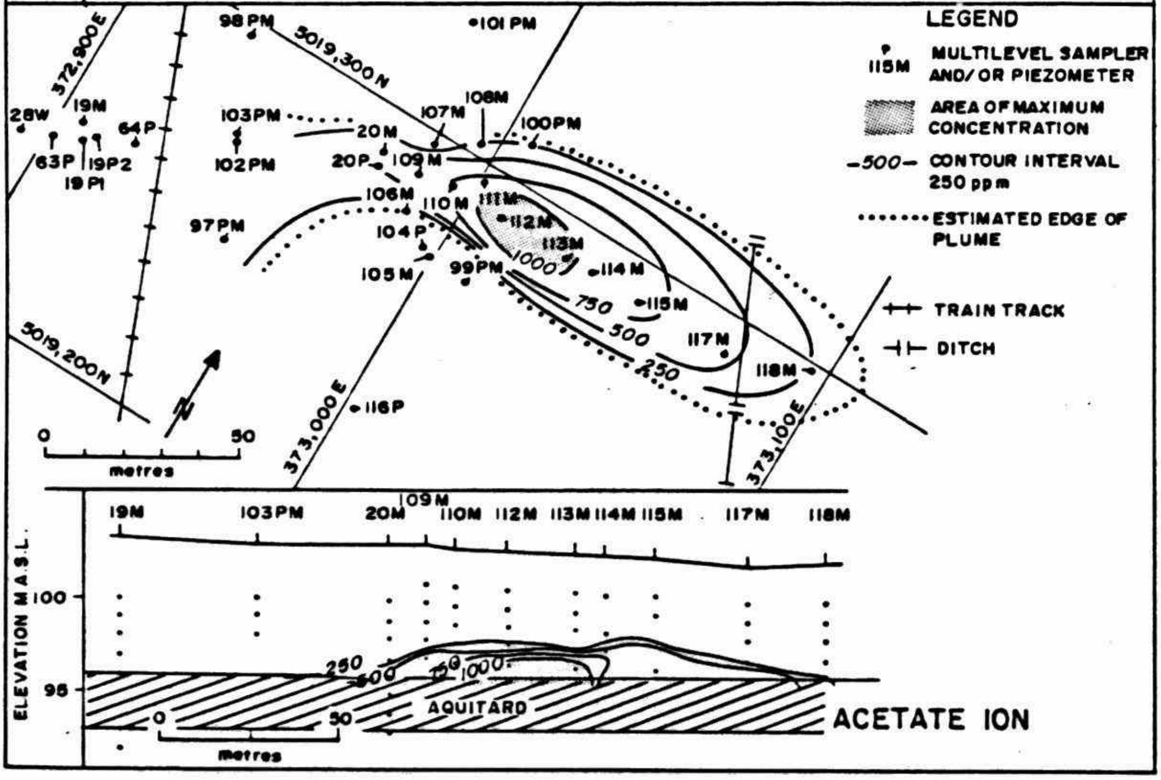


Figure 6: the distribution , in plan and in section, of total alkalinity at the northeast study area.

Figure 7: the distribution , in plan and in section, of acetate at the northeast study area.

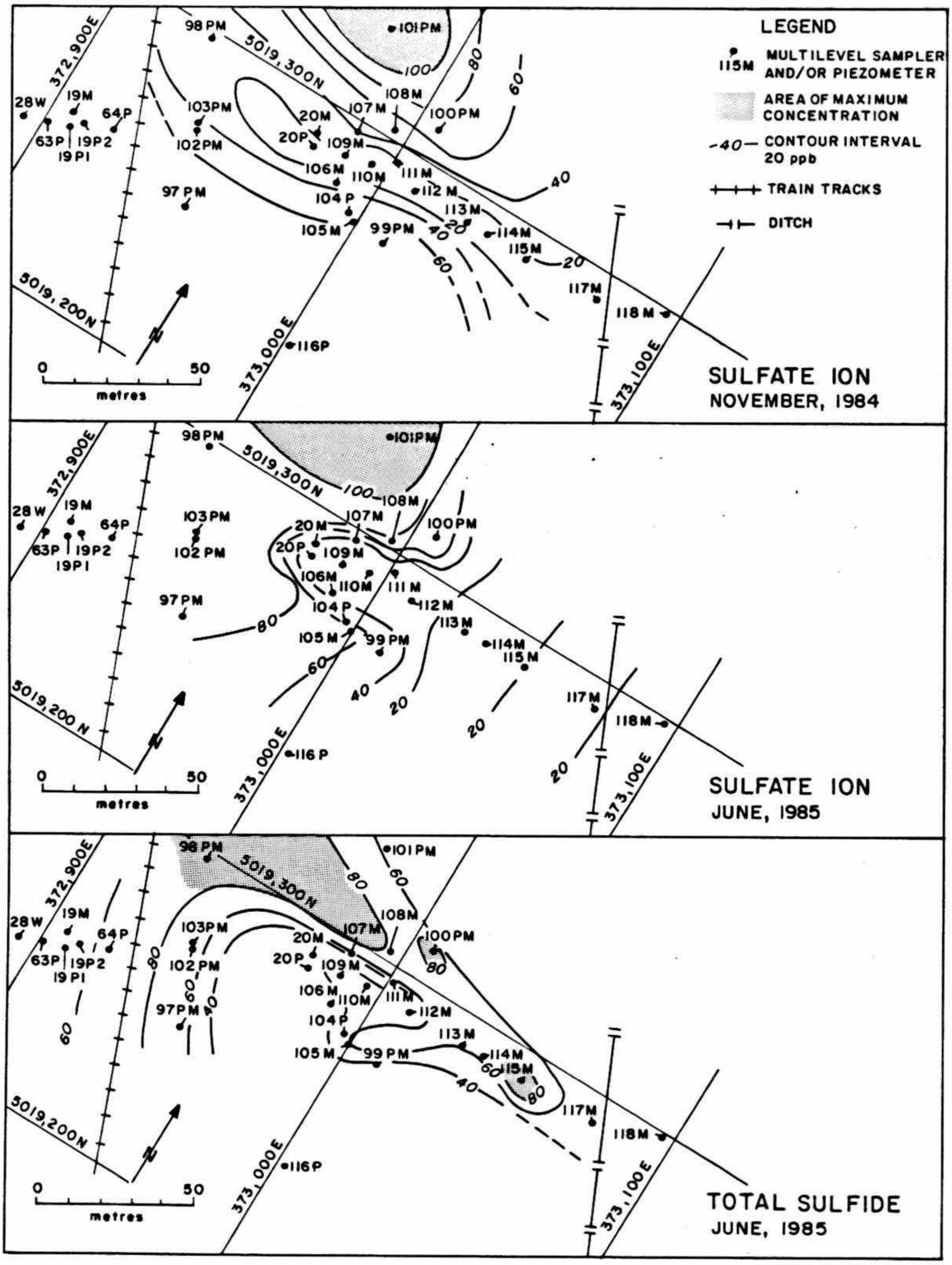


Figure 8: the distributions of sulfate and total sulfide at the northeast study area.

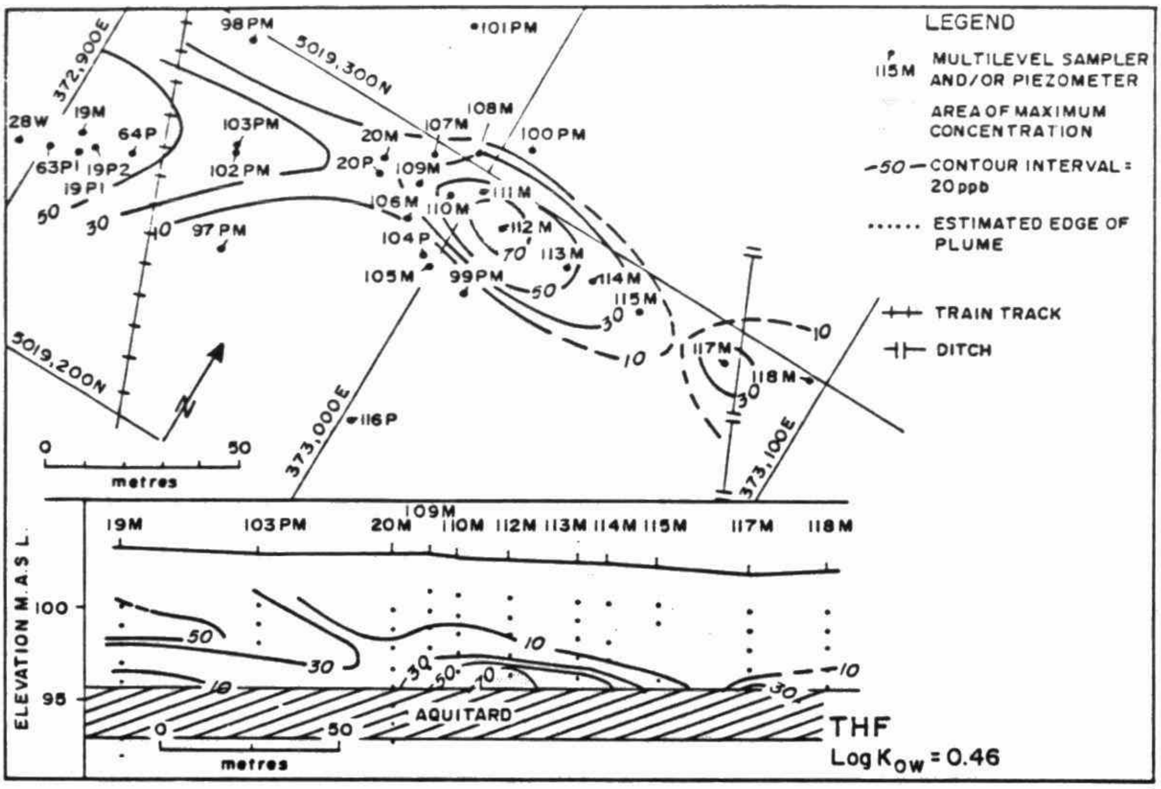
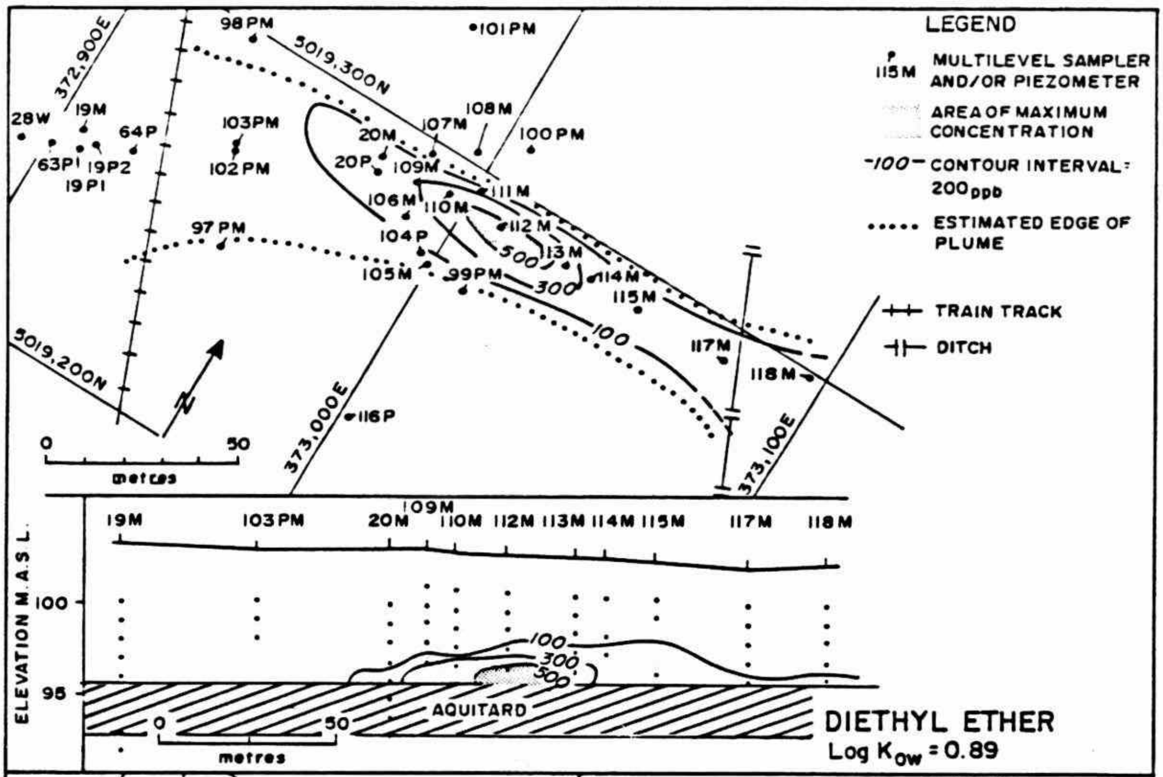

LEGEND
115M MULTILEVEL SAMPLER AND/OR PIEZOMETER
AREA OF MAXIMUM CONCENTRATION
-50- CONTOUR INTERVAL = 20 ppb
...... ESTIMATED EDGE OF PLUME
TRAIN TRACK
DITCH
372,900E
373,000E
373,100E
5019,300N
5019,200N
0 50 metres
ELEVATION M.A.S.L.
100
95
AQUITARD
THF
Log K_OW = 0.46

Figure 9: the distribution , in plan and in section, of tetrahydrofuran at the northeast study area.



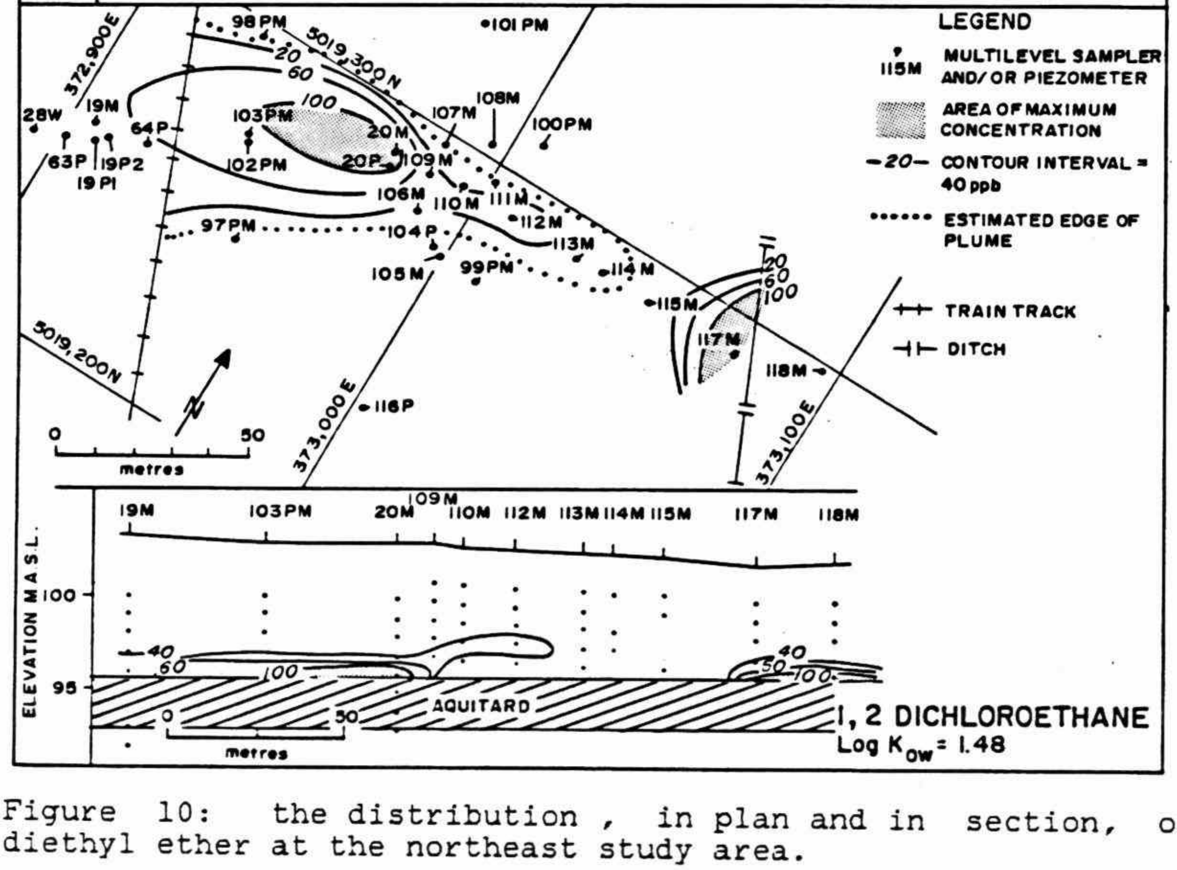
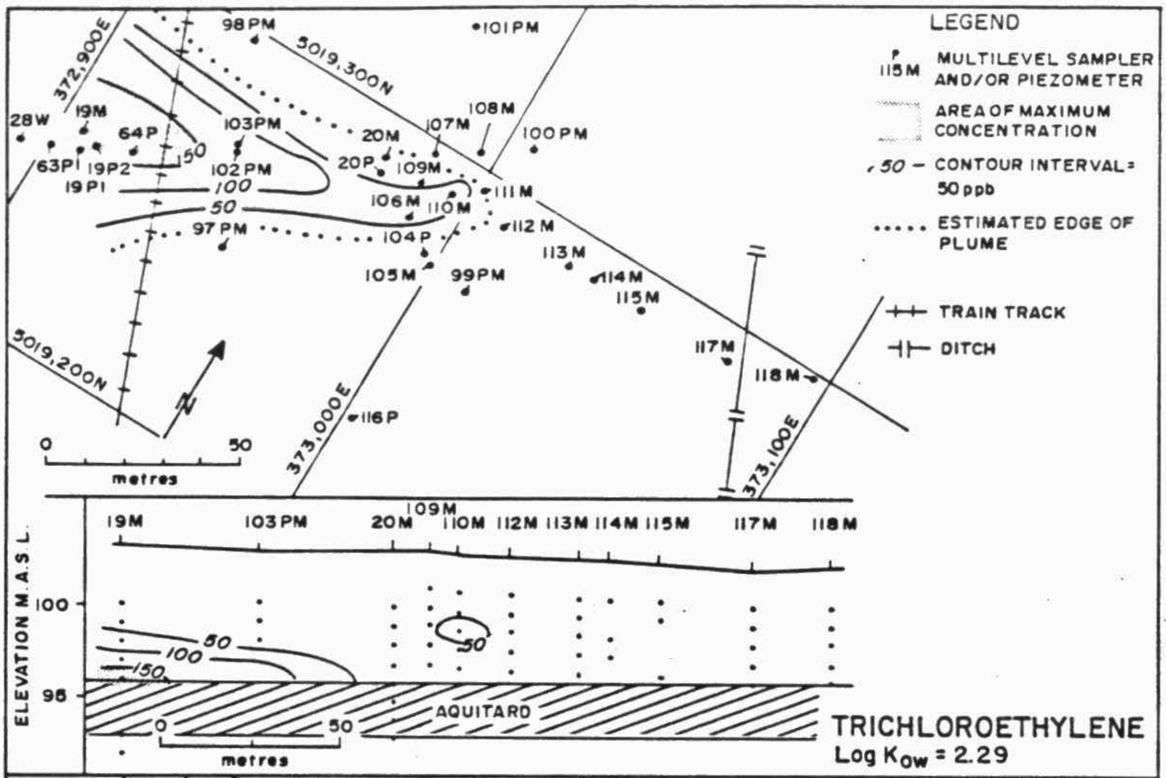


Figure 10: the distribution , in plan and in section, of diethyl ether at the northeast study area.

Figure 11: the distribution , in plan and in section, of 1,2 dichloroethane at the northeast study area.



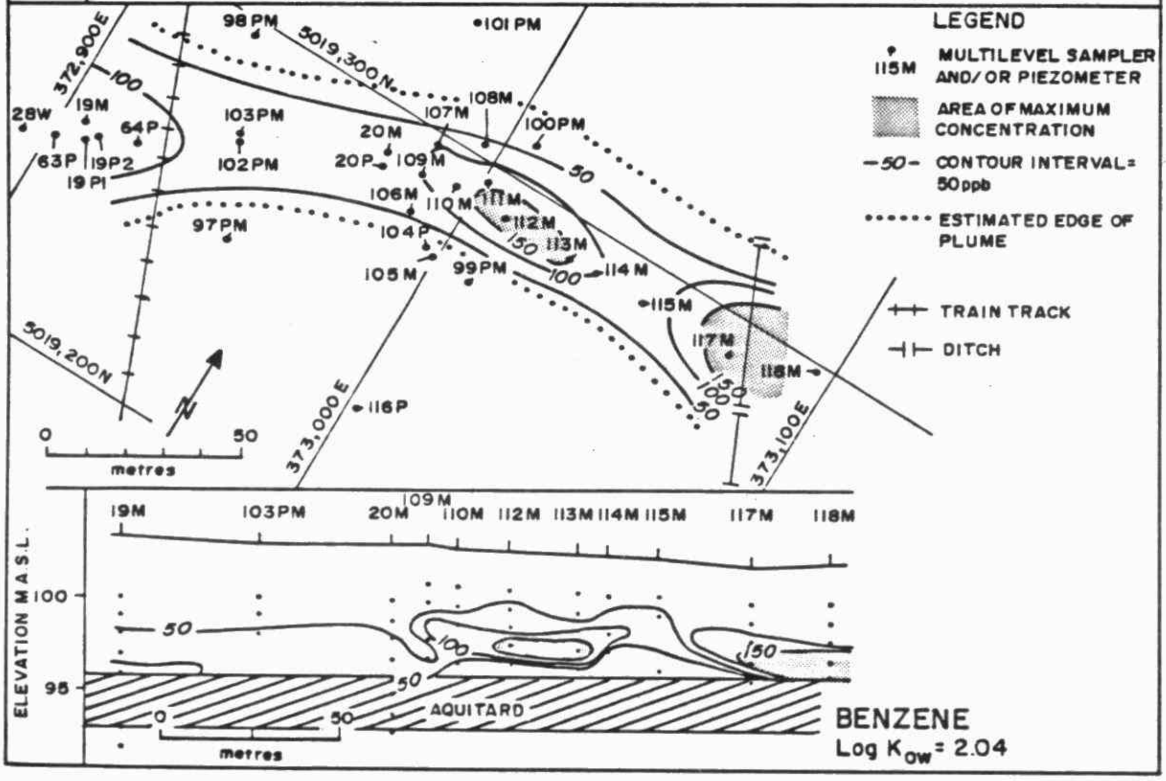
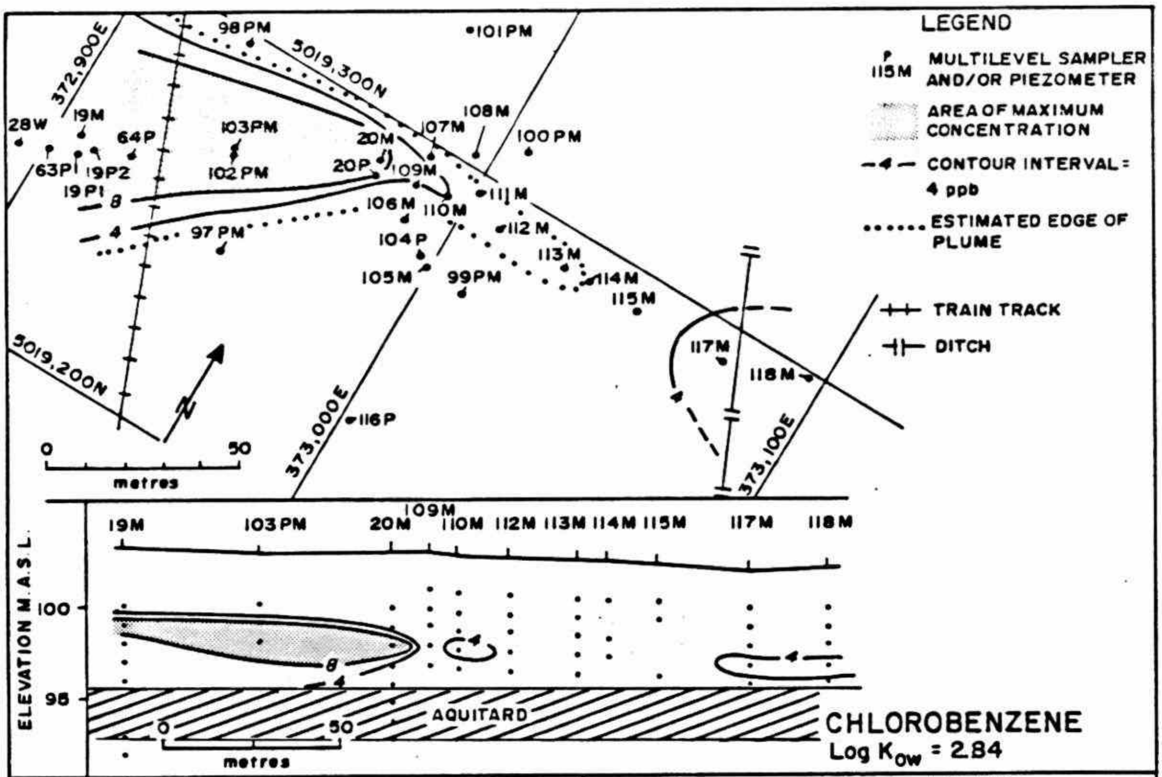


Figure 12: the distribution , in plan and in section, of trichloroethylene at the northeast study area.

Figure 13: the distribution , in plan and in section, of benzene at the northeast study area.



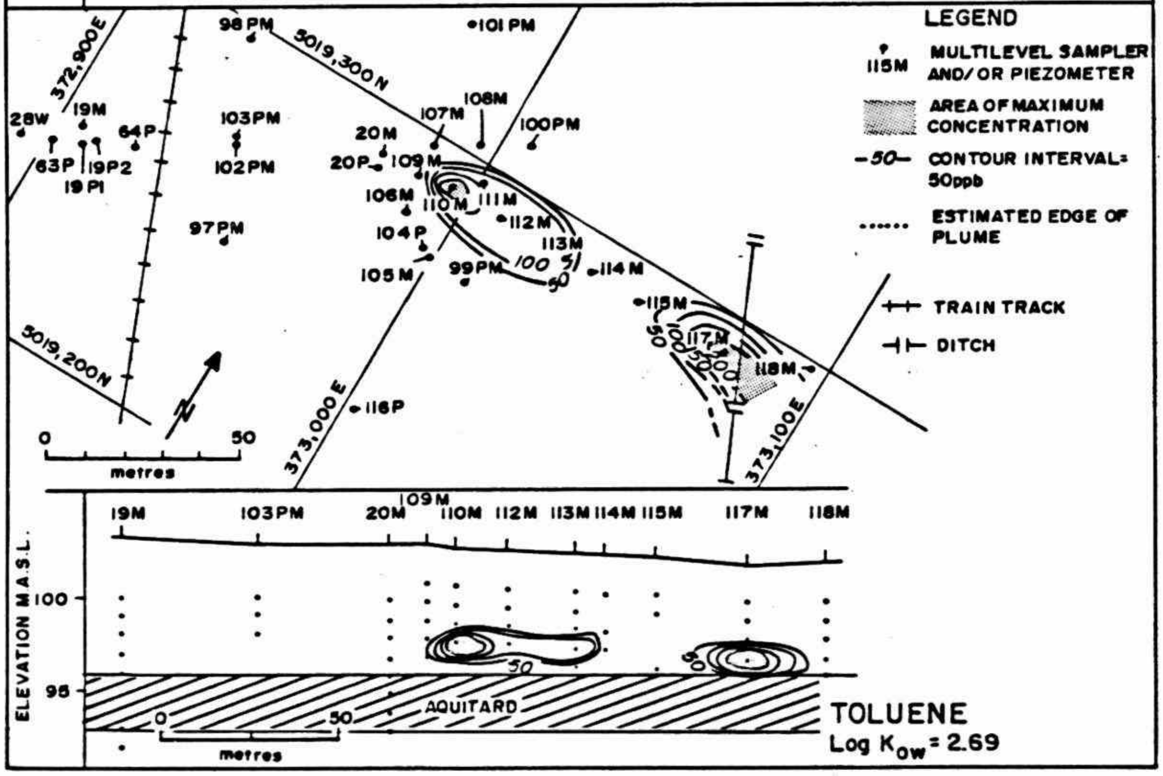


Figure 14: the distribution , in plan and in section, of chlorobenzene at the northeast study area.

Figure 15: the distribution , in plan and in section, of toluene at the northeast study area.

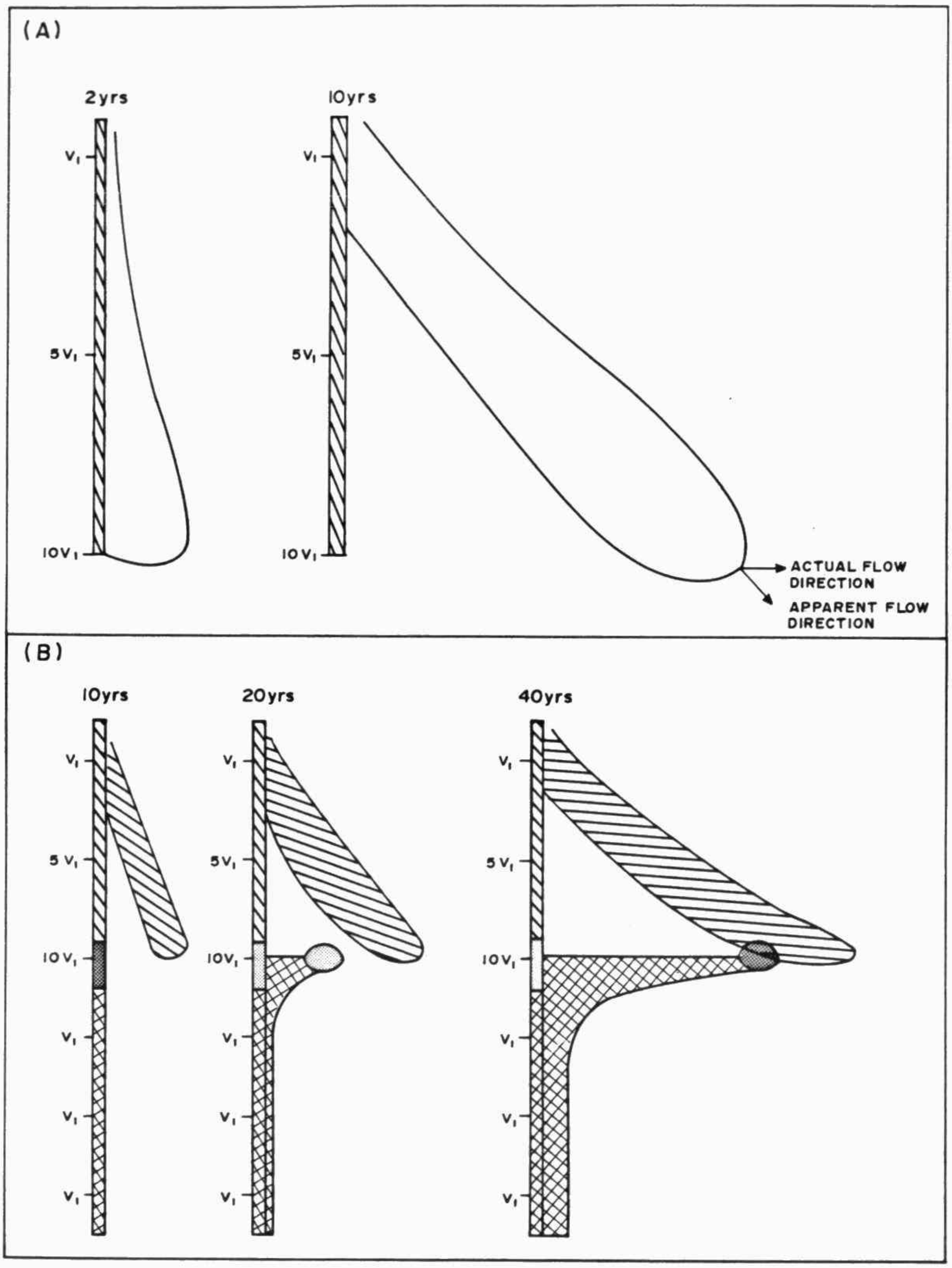


Figure 16 (a): a conceptual model of a contaminant plume emanating from a line source in a variable velocity field (v1 indicates the slowest ground water velocity. (b): a conceptual model showing further development of the plume in figure 16 (a) with a second plume from a point contaminant source introduced after 10 years, in a variable velocity field.

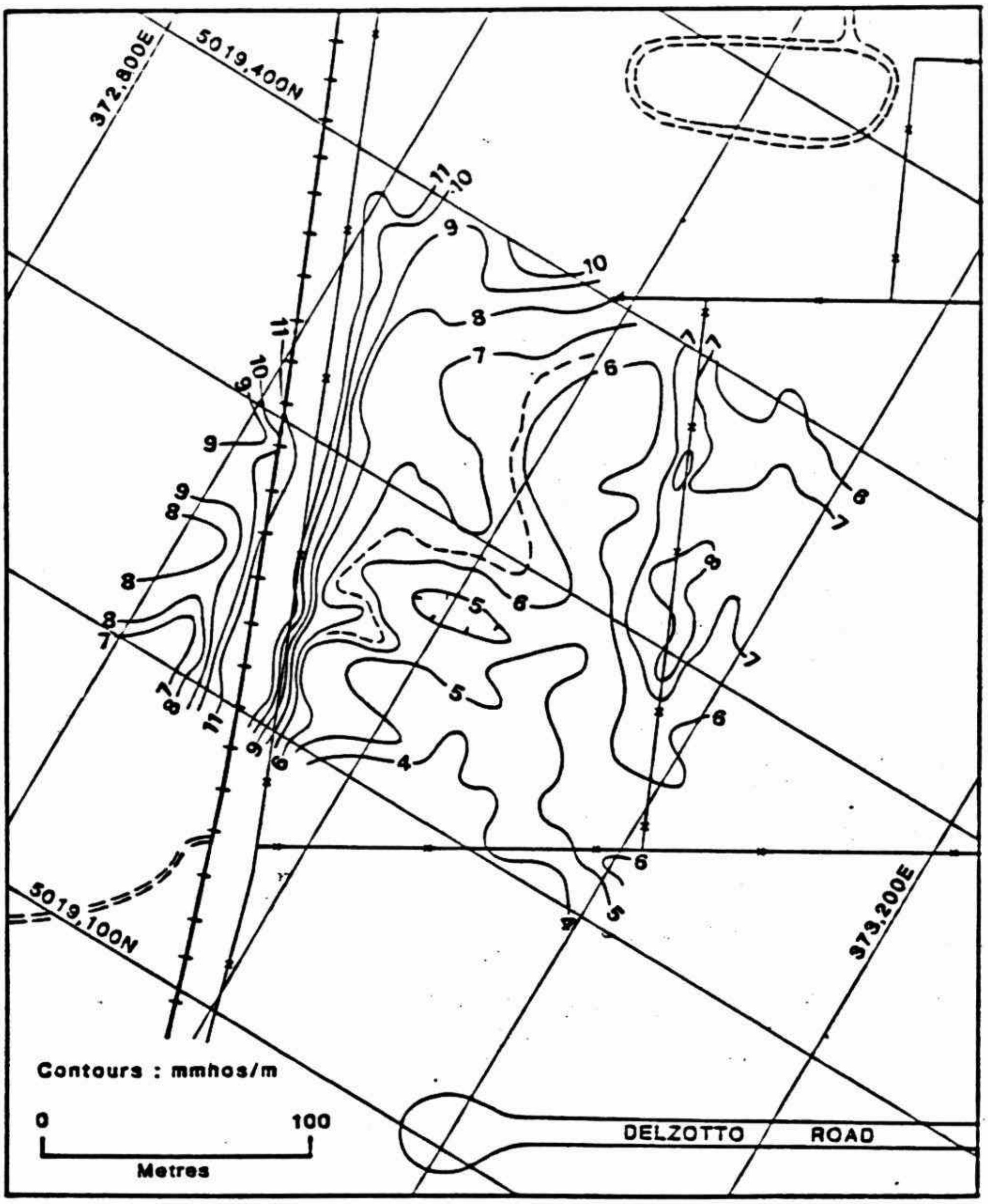


Figure 17: Geonics EM-31 survey of the northeast study area, Gloucester Landfill, 1985 (unpublished, L. Stephens, Geological Survey of Canada, 1985).

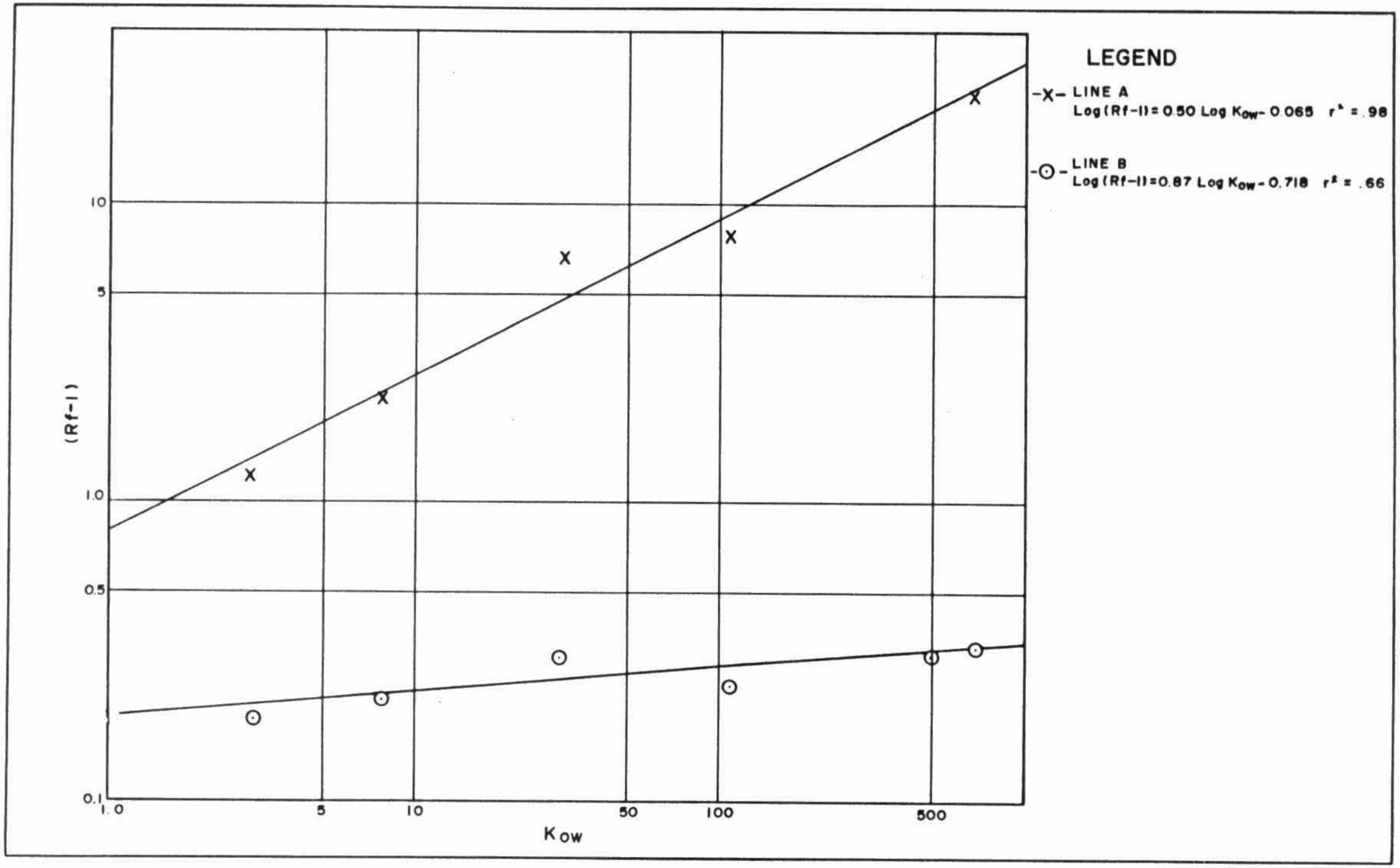


Figure 18: the relationship between retardation factors and octanol/water partition coefficients for volatile organic contaminants at the southeast (line (a) after Patterson _et al._, 1985) and northeast (line (b)) study areas.

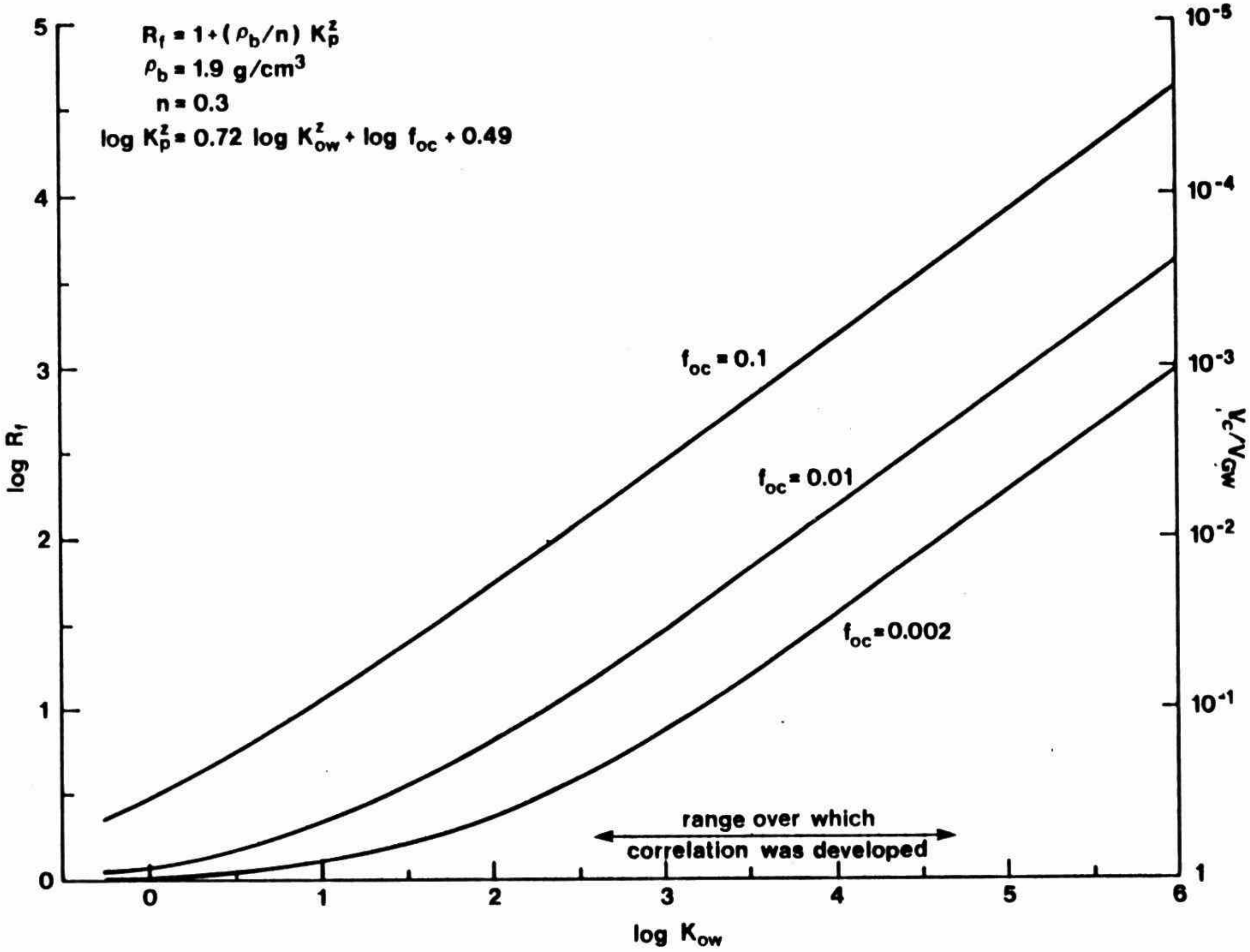


Figure 19: the relationship between retardation factors and octanol/water partition coefficients for sediments of different organic carbon content. As the fraction of organic carbon decreases, retardation factors approach unity (After Jackson *et al.*, 1985).

DESIGN OF GROUNDWATER MONITORING PROGRAMS FOR WASTE LANDFILL SITES

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Department of Civil Engineering, University of Toronto

Key words: Computer Model, Landfill, Groundwater Monitoring, Leachate.

ABSTRACT

A mathematical decision model, incorporating sampling costs, data variability, remedial action costs, and the probability of contamination, has been developed for aiding the design of groundwater monitoring programs. The monitoring program is for detection-type monitoring concerned with observing significant changes in water quality, and where remedial action is initiated upon detection. The tradeoff between periodic monitoring cost and the increased remedial action costs resulting from undetected plume growth is expressed mathematically. The effect on the expected value of the total cost of monitoring and remedial action by decision variables, such as the frequency of monitoring, is investigated.

NO PAPER RECEIVED

AN IN-SITU METHOD FOR DETERMINING RATES OF DENITRIFICATION IN GROUNDWATER

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University of Waterloo

Key words: Denitrification, Groundwater, Nitrates.

ABSTRACT

A survey of nitrate concentrations in unconfined aquifers of Southern Ontario showed that in areas with shallow water tables, nitrate contamination was generally limited to shallow depths below the water table. With the water table at greater depths, nitrates were found to occur at greater depths in the aquifer. The observed distributions have been attributed to the occurrence (or lack of occurrence) of denitrification, and it has been suggested that the extent to which denitrification occurs depends upon the availability of organic carbon.

Previous studies have shown denitrification to be an important process in some aquifers; however, its occurrence is not entirely predictable, and the limiting conditions in the areas where denitrification does not occur are not known. An in-situ method for determining rates of denitrification in groundwater was developed. A column is installed in the field through the centre of hollow-stem augers. Water is withdrawn from the tester, nitrate, chloride and acetylene are added and the solution is re-injected. Chloride acts as a conservative tracer, while acetylene serves as a denitrification block, allowing samples to be analysed for nitrous oxide, to give a positive indication that denitrification is occurring. By determining the rate of nitrate loss, or the rate of increase in N_2O, rates of denitrification can be determined. In addition, nutrients, organic carbon or other additives can be used in the injection water to determine their effect on the denitrification process. The device also appears to have potential for the in-situ study of other biochemical processes such as biodegradation of organic contaminants.

INTRODUCTION

The Department of Earth Sciences at the University of Waterloo has been engaged in studies of the occurrence and distribution of nitrate in groundwater associated with agricultural water sheds for almost ten years. Results of these studies are reported in Gillham and Cherry (1978), Egboka (1978), Hendry et al. (1982), Gillham et al., 1984 and Trudell (1985). Generally, surveys of nitrate concentration have shown high values to be associated with groundwaters in unconfined sandy aquifers in areas of intensive agricultural production. Of perhaps greater interest, detailed studies have shown that where the water table occurs at depths of less than about 3 to 4 m below ground surface, nitrate contamination is limited to depths of 2 to 3 m below the water table. Generally, sharp decreases in nitrate concentration, dissolved oxygen and redox potential, all occur at relatively shallow depths below the water table. This evidence plus detailed tracer tests and geochemical studies conducted by Trudell et al. (1985) shows the loss of nitrate with depth to be the result of denitrification; the biochemical conversion of nitrate (NO_3^-) to nitrogen gas (N_2), with the conversion to nitrous oxide (N_2O) as an intermediate step. In areas with deeper water tables, there appears to be a gradual decrease in nitrate concentration with depth; however, the trends are not as distinct as in areas with shallow water tables, and generally do not appear to be accompanied by similar trends in the redox indicators, suggesting that in these areas, denitrification is not a significant process.

Denitrification is a potentially beneficial process in groundwater in that it converts a recognized contaminant (NO_3^-) to non-toxic nitrogen gas (N_2). Recognizing areas where denitrification is likely to occur could influence recommended land-use practices, and understanding the factors that determine the occurrence of denitrification could potentially lead to practices that would tend to promote the denitrification process.

Denitrification requires the presence of appropriate bacterial populations, an organic carbon source of energy for the bacteria, and reducing conditions. We have postulated that the characteristic nitrate profiles observed for shallow and deep water table conditions is related to the dissolved organic carbon content of the groundwater. In particular, it is suggested that under shallow water-table conditions, relatively large amounts of labile organic carbon are carried into the groundwater zone by infiltrating water. Once removed from the source of oxygen, the atmosphere, continued biodegration removes the oxygen from the water, resulting in reducing conditions and the occurrence of denitrification. Under deep water-table conditions it is suggested that most of the labile organic carbon is oxidized before reaching the water table. As a result, oxidation of organic carbon below the water table is a very slow process, leaving measureable concentrations of dissolved oxygen, and thus the denitrification process does not proceed.

The general objectives of the present study were to evaluate the distribution of nitrate in a shallow sandy aquifer at Alliston, Ontario, to develop methods of well development that would result in improved quality of domestic wells in the aquifer, and to evaluate the factors that control the occurrence of the denitrification process.

This paper is related to the final objective, the evaluation of factors that affect the occurrence of denitrification, and specifically, describes the construction and testing of a device that was developed for measuring in-situ rates of denitrification in saturated geologic materials. The device can be used to measure potential rates of denitrification under natural hydrogeologic conditions and can also be used to examine the effect of various additives such as organic carbon on the rate of denitrification.

Though developed specifically for studies of denitrification, we believe the device and procedures to be more generally applicable to the study of a variety of biochemical processes that may occur in groundwater. In particular, it may be useful in studies of rates of biodegradation of organic contaminants in groundwater.

TESTER DESIGN

The testing device has progressed through several design stages and modifications. The design presented here is the most recent, though the data to be presented in a later section was actually collected from an earlier though similar model.

A schematic of the tester is shown in Figure 1. The barrel of the tester consists of a length of stainless-steel pipe 60 cm long, 6.4 cm inside diameter and 0.63 cm wall thickness. The bottom end is sharpened to allow for easy penetration of the geologic material, while the upper end is threaded for attaching to the end-plate section.

The end-plate section consists of a 12 cm length of identical stainless-steel pipe, with the end plate welded into the bottom end. Grooves are cut in the lower surface of the end plate, and covered with 200-mesh stainless-steel screen material. A tubing connector located on the top of the end plate allows for the addition or removal of fluids from the barrel of the tester through the screened surface of the end plate.

A sampling tube, 10 cm long and 0.62 cm O.D. is threaded into the centre of the bottom surface of the end plate. This tube is connected through a second tubing connector on the top of the end plate to flexible tubing that leads to ground surface. Fluids are withdrawn from the small screened interval near the bottom of the sampling tube. A stainless-steel head for attaching the tester to drill rods is threaded onto the top of the end-plate section.

INSTALLATION AND OPERATION

The tester was designed for installation through the annulus of 10 cm I.D. hollow-stem augers. Using a trap-door cutting head, such as that described in Goodwin and Gillham (19xxx), to prevent the movement of soil and water into the augers without the use of foreign water, the augers are advanced to the desired depth of installation. The tester is then lowered through the augers until it contacts the doors of the cutting head. Holding the tester in place while lifting the augers a few centimeters forces the doors open, allowing the tester to penetrate the geologic material. By pushing and vibrating the drill rods, the tester is advanced until the barrel is completely filled with the geologic material. Though this procedure would cause some degree of physical disturbance of the sample, in that foreign water is not used and exposure of the sample to the atmosphere does not occur, the geochemical integrity of the test material (the material inside the barrel) should be preserved.

In principle, groundwater can be withdrawn through the tube connected to the screened surface of the end plate; tracers, contaminants or additives can be added and the water re-injected. Samples can then be collected from the sampling tube at appropriate intervals of time to determine changes in concentration over time. Though samples could also be collected from the end plate, the dead-volume of the sampling tube is much smaller, requiring less flushing in order to obtain a fresh sample.

In the tests reported here, nitrate and acetylene were added to the injection water. During denitrification, nitrate is normally converted to nitrous oxide then to nitrogen gas. Acetylene has been shown to block the conversion of nitrous oxide to nitrogen gas and thus the presence of nitrous oxide is a positive and conclusive test for the occurrence of denitrification, and rates of denitrification can be calculated from the rate of increase in the N_2O concentration.

FIELD TESTS

Two field tests are described here, one at a site where denitrification was believed to be occurring (Rodney site), and the second at a site where denitrification was not believed to be occuring (Alliston site).

Rodney Site

The Rodney site, approximately 80 km south-west of London, Ontario, was the same site as that described in Trudell et al. (1985), and was chosen because of the strong indications that denitrification was occurring at this location. Figure 2 shows nitrate and dissolved oxygen profiles obtained from a multilevel sampling device installed at the site. As expected under shallow water-table conditions, the DO shows a characteristic decline to near-zero values at shallow depths below the water table. In that the nitrate values were all below the level of detection, the characteristic nitrate profile was not observed.

Because of the shallow depth to the water table, installation was performed by hand-augering to just below the water table, then driving the tester into the soil using a Cobra vibrating hammer.

After installation, the tester was pumped for about half an hour to ensure that natural formation water filled the bore of the device. This procedure was followed to ensure that the formation water could not have become oxygenated during the installation procedure. A 2.5 l glass bottle was then flushed several times with formation water pumped directly from the device. The bottle was then filled with 2.3 l of formation water to which a measured amount of potassium nitrate was added. The solution was then purged for about one and one half hours by slow bubbling with acetylene gas. This solution was then reinjected. After pumping all the solution down the device the injection and sampling lines were clamped off. This was designated as the starting time of the experiment. The 2.3 l of solution was approximately three pore volumes of the device used at Rodney, ensuring that all the pore water in the bore of the device was the injection solution. The initial nitrate concentration in the injection solution was 3.2 mmole/l (20 mg/l NO_3^--N)

Samples of the injection solution were taken at daily or sometimes greater than daily intervals. Samples for nitrous oxide and acetylene analysis were collected in 50 ml plastic syringes connected directly to the sampling tubes. Before sample collection about 5 ml of water was collected and discarded. This was followed by collection of a 10 ml sample. To minimize degassing, care was taken to limit the vacuum on the sampling lines to only that required to induce flow. Unfortunately, even with extreme care some degassing did occur. Generally a sample had about 10 ml of water and 5 ml of headspace. Because of the anlytical method, the integrity of a sample with a large headspace was suspect. Samples for gas analysis were collected in duplicate and acidified with phosphoric acid to suspend biological activity in the syringes. The syringes were stored in a container of water to minimize gas diffusion through the syringe walls and transported back to the laboratory for analysis. For nitrate analysis 10 ml samples were collected in 20 ml plastic syringes. These samples were stored and transported in cold water and refridgerated on arrival at the laboratory.

Nitrous oxide and acetylene samples were analyzed every few days using a Fisher Model 29 Gas Partitioner. The nitrate samples were analyzed using a Dionex Ion Exchange Liquid Chromatograph.

Results of the test are given in Figure 3. The nitrate concentration shows a rapid decline from the initial concentration starting at about 265 hr after initiation of the test. Assuming that the decline in the nitrate concentration was entirely due to denitrification, then the maximum rate of denitrification (at about 320 hr) was 0.05 mmole/l/hr. Though high, this value falls within the range of values reported in the literature (0.0019 to 0.18 mmole/l/hr.) as given by Trudell et al., 1985.

Nitrous oxide was detected at about the same time that the decline in nitrate was first noted, and the concentration of N_2O continued to increase as the nitrate concentration decreased. The rate of N_2O production was significantly less than the rate of NO_3^- disappearance, and the final N_2O concentration could only account for about 30% of the nitrate that was lost. This apparent loss of nitrogen may be associated with the analytical problems caused by the large head space in the samples, of if the acetylene block was not complete, then some of the N_2O may have been converted to N_2. The N_2O data was useful in providing proof that denitrification was occurring; however, unless the apparent loss of nitrogen can be resolved, it appears that rates of denitrification can be calculated more reliably from the rate of nitrate loss.

It should be noted that the injected slug of water contained significant oxygen contamination (data not shown) and that denitrification did not proceed until the DO values approached zero. In the absence of DO contamination, it is quite likely that the delay before denitrification proceeds would be much less than the 265 hr observed here.

Alliston Site

The hydrogeologic setting in the vicinity of the Alliston site is given in Gillham et al. (1984). Generally it consists of a sandy aquifer, with the water table varying from depths below ground surface of about 2 m to 10 m. Profiles of NO_3^- and DO at the particular site chosen for this test are given in Figure 3. Both NO_3^- and DO show a gradual decline in concentration with depth. In that the DO values remain high, it is quite unlikely that the rapid decline in NO_3^- at a depth of about 15 m is the result of denitrification.

The in-situ device was installed at a depth of about 4.4 m below ground surface and 0.3 m below the water table. Procedures similar to those described for the Rodney site were used.

Because of the high initial dissolved oxygen concentration, it was expected that denitrification would not occur, and thus that the nitrate concentration would remain relatively constant for the duration of the experiment and no nitrous oxide would be detected. As shown in Figure 5, this was clearly not the case. The presence of N_2O provides evidence that denitrification was occurring, and the rate of decline in the nitrate concentration indicates rates of denitrification comparable to those observed at Rodney.

Various hypotheses were proposed to explain the unexpected results; however, similar results at a second site where denitrification was not expected to occur raised serious questions about the procedure. A careful investigation of the various steps in the procedure showed that the addition of acetylene to the water resulted in a substantial increase in the dissolved organic carbon content (in excess of 100 mg/l). This increase was subsequently traced to the acetone used by the manufacturer to stabilize the acetylene in the storage tank. When injected into the tester, oxidation of the acetone would result in reducing conditions that would allow denitrification to proceed.

We have found that slowly bubbling the acetylene from the tank through a series of three or four water traps will effectively remove the acetone, and other refinements in the sample collection and analytical procedures should result in improved nitrogen balances. A further series of tests, both at Rodney and at a non-denitrifying site are currently in progress.

COMMENTS

Because of the problems associated with the acetone contamination, the only reasonable conclusion that can be drawn from the preliminary results is that the necessary bacterial populations for denitrification were present at both sites. No reliance can be put in the measured rate of denitrification at Rodney, and certainly the results at Alliston can not be considered representative of the in-situ conditions. In spite of the difficulties in the preliminary experiments, caused primarily by the unrecognized source of organic contamination, the device has demonstrated a great potential for being able to evaluate in-situ denitrification rates.

In the series of tests currently in progress at an apparently non-denitrifying site, a control test (natural DO, nitrate and acetylene in the injection water), a low DO test (identical to the control but with the DO removed), and a high DOC (identical to the control but with glucose added), are being conducted. Our expectation is that denitrification will not occur in the control but will occur in the high DOC test. This would tend to confirm that DOC is the limiting factor on the occurrence of denitrification.

Though useful in denitrification studies, the tester may be more generally applicable to a wider range of biological processes. In particular, it may be useful in studying rates of biodegradation of organic contaminations in a variety of hydrogeochemical conditions. For example, benzene, toluene and xylene, soluble constituents of gasoline, are considered to biodegrade readily under oxidizing conditions, but to be relatively non-degradable under reducing conditions; however, there are no convenient methods for measuring in-situ rate constants. Though laboratory methods are available, they are generally performed on samples that are both physically and chemically disturbed raising serious questions regarding the field applicability of the results. In that reducing conditions are particularly difficult to maintain, the applicability of laboratory results to reducing hydrogeologic environments is particularly questionable.

The in-situ device is presently being used to measure rates of biodegradation of benzene, toluene and xylene at two sites in the sand aquifer at Canadian Forces Base Borden. One site is in an oxidizing zone and the other in a reducing zone. These tests were initiated very recently, and no results are available at the present time.

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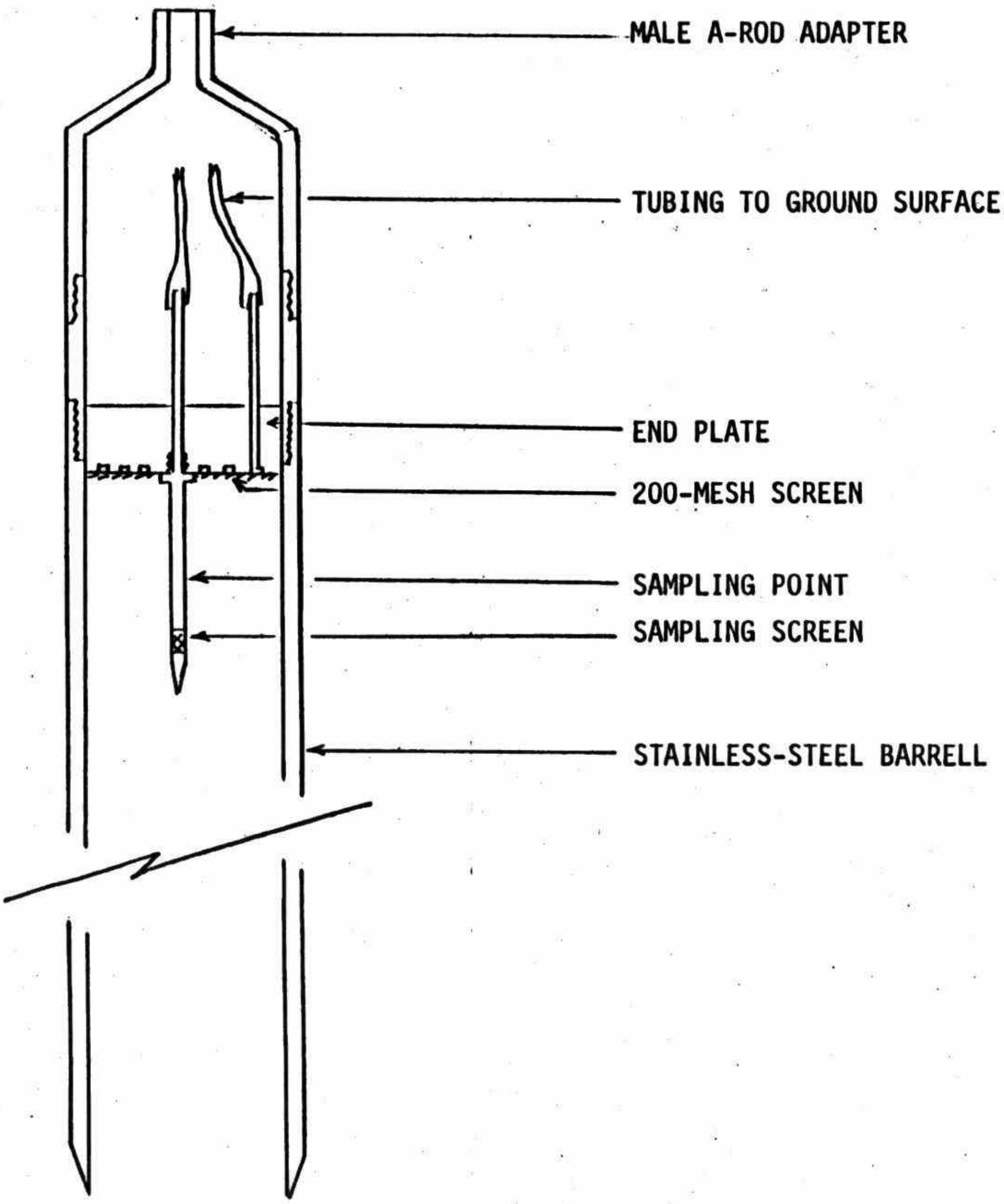


Figure 1. Schematic of the in-situ testing device (not to scale)

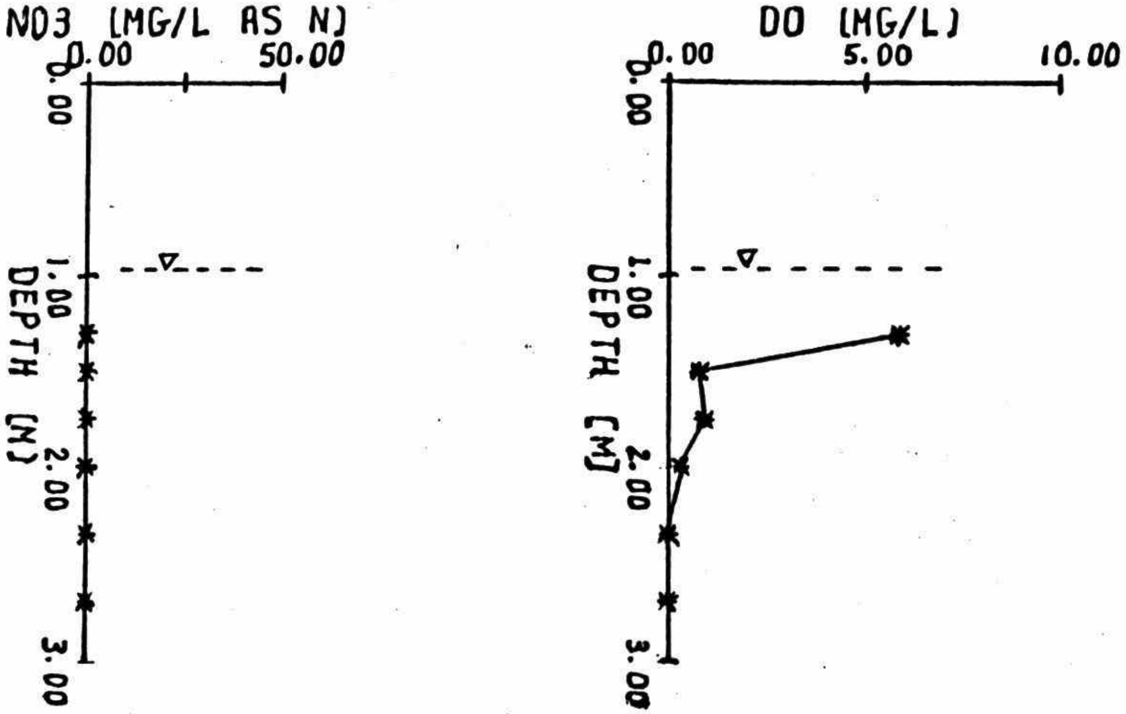


Figure 2. Nitrate and dissolved oxygen profiles at the Rodney site

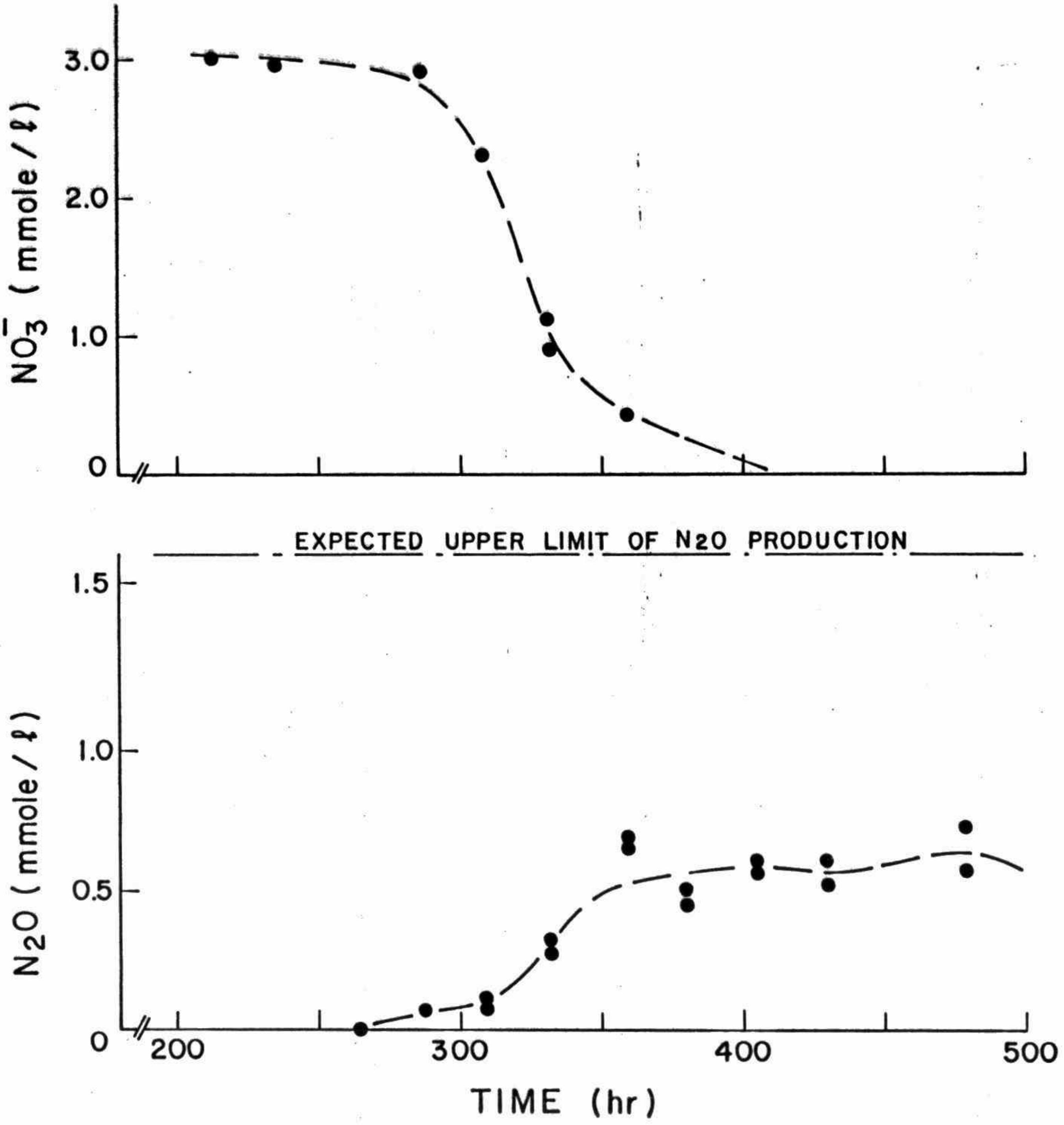


Figure 3. N_2O and NO_3^- versus time at the Rodney site

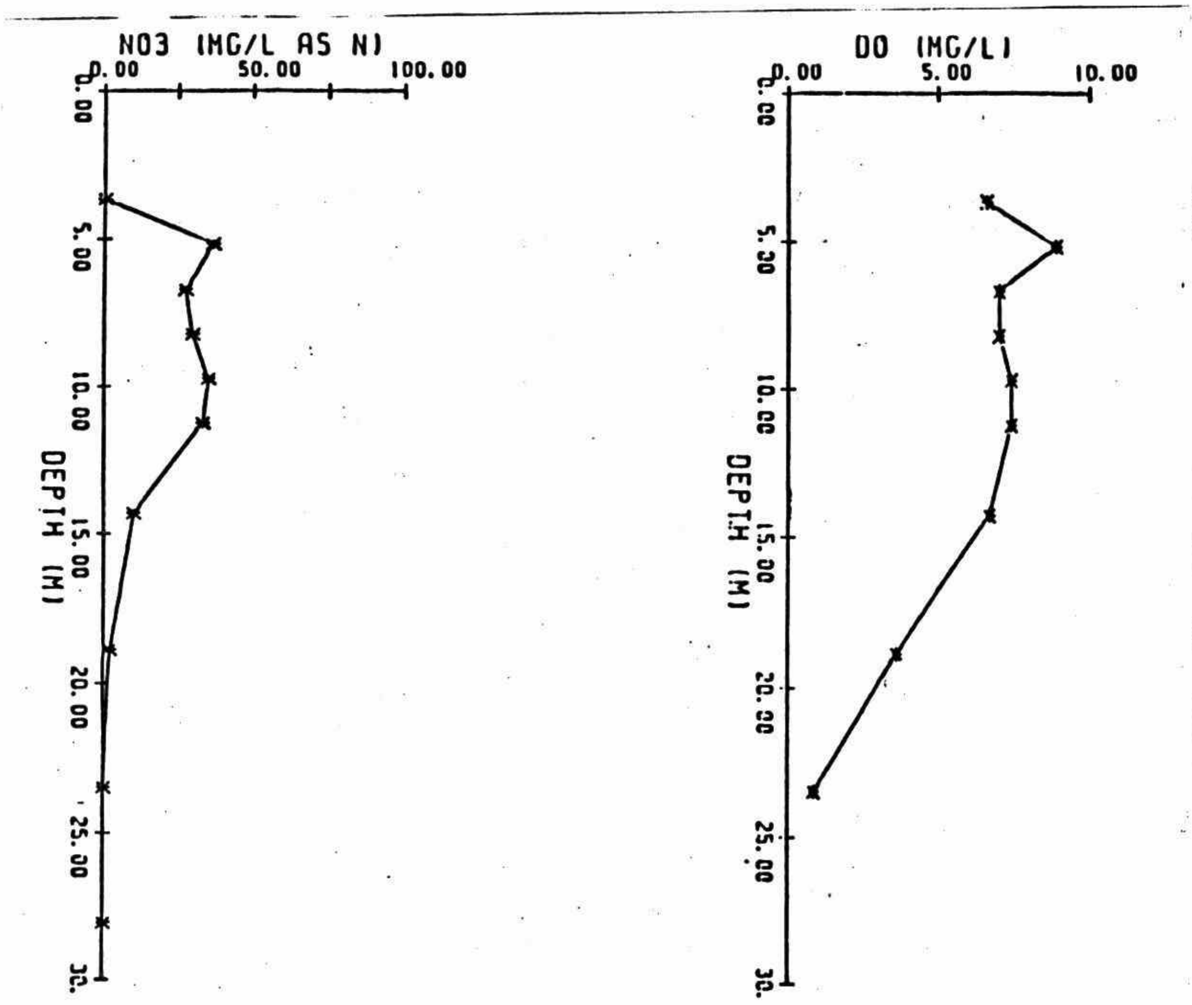
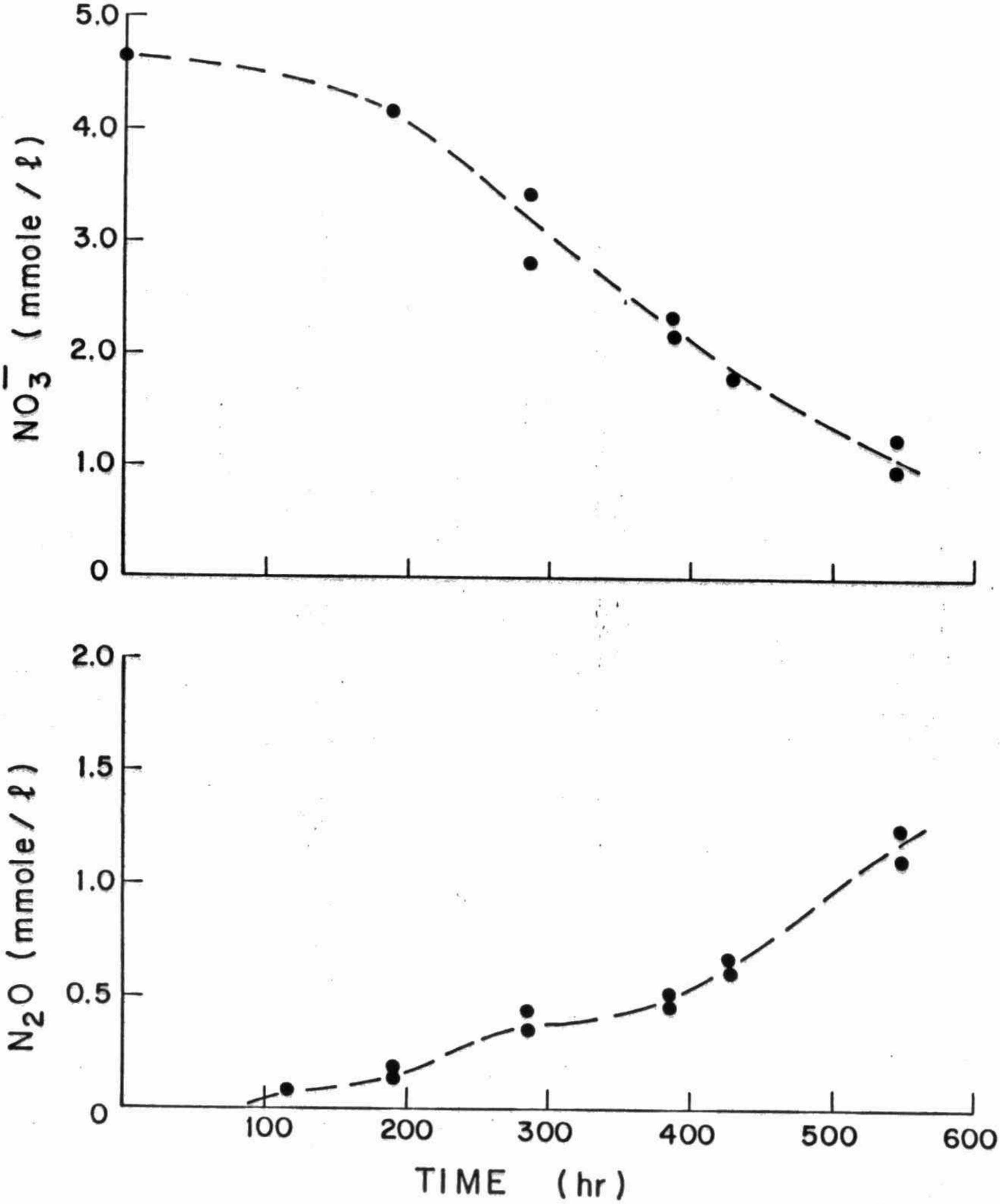


Figure 4. Nitrate and dissolved oxygen profiles at the Alliston site


5.0
4.0
3.0
2.0
1.0
0
NO_3^- (mmole / ℓ)
2.0
1.5
1.0
0.5
0
N_2O (mmole/ ℓ)
100
200
300
400
500
600
TIME (hr)

SELECTION OF AERATION DEVICES

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Key words: Aeration Devices, Activated Sludge, Sewage Treatment.

ABSTRACT

Selection of aeration devices for activated sludge treatment plants is usually made on the basis of the equipment costs and the basic technological factors: oxygenation capacity and oxygenation economy (energy consumption) values provided by the manufacturers of these devices. The mixing characteristics and the replacement and maintenance requirements for these devices are taken into consideration less often. Environmental factors such as stripping and cooling abilities, formation of aerosols, and noise generation are only occasionally analyzed. All of these latter factors, in addition to their technological meaning, are related to the health problems of operational personnel at wastewater treatment plants, and of communities in the vicinity of the plants. This study presents a comprehensive and systematic analysis and evaluation of all aspects of aeration devices to facilitate the selection of these devices for specific application. A review of the problems associated with different aeration systems is given and a "checklist" for selection of aeration systems is formulated. The proper selection process of aeration devices for a specific activated sludge treatment facility should be a multi-stage exercise, including (a) client preferences and analysis of the selection restrictions due to local factors and factors arising from the plant design; (b) equipment pre-selection on the basis of energy and capital cost considerations; (c) detailed analysis of technological factors involved in the operation of the aeration devices considered (oxygenation capacity, oxygenation economy and mixing performance); (d) detailed analysis of environmental factors (stripping, aerosol formation, cooling, and noise generation); and (e) final and comprehensive cost analysis of acceptable aeration systems, comprising elements added to correct or improve the technological and/or environmental performance of the devices. Each stage of the selection process will alter the preferences among the available devices and will shorten the list of these devices, but the last stage will bring the final recommendations.

SELECTION OF AERATION DEVICES

J.J. Ganczarczyk

1. INTRODUCTION

Available information on aeration devices for the activated sludge process is dispersed among various scientific and technical publications and reports, and the data provided by manufacturers of these devices. This information is often confusing as it can be presented in different ways and sometimes is subject to specific editing.

Selection of aeration devices for activated sludge treatment plants is usually made on the basis of the equipment costs and the basic technological factors: oxygenation capacity and oxygenation economy (energy consumption) values provided by the manufacturers of these devices. The mixing characteristics and the replacement and maintenance requirements for these devices are taken into consideration less often. Environmental factors such as stripping and cooling abilities, formation of aerosols, and noise generation, are only occasionally analysed. All of these latter factors, in addition to their technological meaning, are related to the health problems of the operational personnel at the wastewater treatment plants and of the communities in the vicinity of the plants.

This report presents a systematic analysis and evaluation of all aspects of aeration devices to facilitate the selection of these devices for specific applications.

2. OXYGENATION CAPACITY

The ability of aeration devices to introduce oxygen into solution in the mixed liquor, is determined in the form of the overall oxygen mass transfer coefficient (K_La) or, more often, as the oxygenation capacity, expressed in mass terms (pounds or kilogram) of oxygen transferred into solution per unit of time under the testing conditions. These testing conditions include:

a) the tested aeration medium (clean water, sewage, industrial wastewater, respective mixed liquors, etc.),
b) the size of the testing tank, and
c) the mode of operation of the device tested.

The influence of the aeration medium on the aeration kinetics may be quite substantial, and can be expressed by the coefficients alpha and beta. The first of those coefficients directly describes the changes in the oxygen transfer kinetics, and the second one, the changes in the oxygen transfer driving force (difference in oxygen saturation values). It must also be noted that the alpha coefficients depend heavily on the type of aeration device applied, and generally are much lower (less efficient oxygen transfer) for fine-bubble air aeration than for mechanical surface aeration.

Although substantial efforts have been devoted to scaling-up the effects of aeration devices, it is still more an art than a science, and caution should be exercised in applying the findings of aerator testing, even in a large pilot-scale, to full-scale operation.

The mode of operation of the aeration device tested also influences the results of the test. If an aeration device is put into operation to find its aeration capacity, the initiation of the operation will consume more energy than the normal operational requirement, and will produce a higher oxygen transfer than may be expected under normal operation of the unit. Such over-estimations of oxygenation capacity may be in the range of 20% or more, depending on the size of the unit tested and the hydrodynamic properties of the testing tank. Therefore, for practical purposes, the aeration kinetics should be measured only under operational conditions.

For testing of the aeration kinetics (aeration capacity), several methods may be used. They may be based on:

a) aeration of the deoxygenated aeration medium with a chemical deoxygenation preceding the aeration test (e.g. Black, 1982);
b) stripping from the aeration medium an excess of oxygen

introduced as hydrogen peroxide (Kayser, 1979), or stripping biochemically-inactive trace gases from it, and

c) measuring the composition of off-gases (oxygen uptake from the aeration air) for the deoxygenated medium, or medium under biological treatment conditions (for air bubble aeration only).

It should be noted that, to date (Fall 1985), a standard procedure for aeration testing under operational conditions has not yet been fully developed. The ASCE (American Society of Civil Engineers) Standard for "Measurement of Oxygen Transfer in Clean Water" was released only recently (1984). This standard was developed to measure the rate of oxygen transfer from diffused gas and mechanical oxygenation devices to relatively large volumes of water, typical of those found in the activated sludge wastewater treatment process. The test method is based on removal of dissolved oxygen from the water volume by sodium sulfite, followed by reoxygenation to near saturation level. The dissolved oxygen inventory of the water volume is monitored during the reaeration period by measuring dissolved oxygen concentrations at several points, selected so that each point senses an equal tank volume. This method specifies a minimum number, distribution and range of dissolved oxygen measurements at each point. The data obtained at each determination point are analysed by a simplified mass transfer model to estimate the apparent volumetric mass transfer coefficient, and the oxygen saturation concentration. Non-linear regression (Stenstrom et al., 1981) is employed to fit the model to the dissolved oxygen profile measured at each point during reoxygenation. In this way, estimates of the transfer coefficient and the saturation value are obtained at each point. These estimates are adjusted to standard conditions and the standardized oxygen transfer rate (mass of oxygen dissolved per unit of time in clean water under standard conditions of temperature and pressure at an hypothetical concentration of zero dissolved oxygen) is obtained as the product of the average adjusted transfer coefficient, the average adjusted saturation value, and the tank volume. A procedure based on the clean water test results is prescribed for estimation of oxygen transfer rates in "dirty" water under process conditions. In this standard procedure, various components of power consumption are defined and methods for measurement of gas rate and power consumption by the oxygenation device are given. It is hoped that this standard will be used by all manufacturers of the equipment in the preparation of specifications for compliance testing and in the development of information on the performance of the equipment.

The accuracy and precision of the application of the ASCE oxygen transfer test, both in replicate shop and plant-scale, was recently studied by Baillod et al.(1984), and was compared with the krypton stripping test. Both its precision and accuracy proved to be very good.

The radioactive tracer method for testing aeration capacity usually involves the application of radioactive krypton-85 gas for evaluation of oxygen transfer, and tritiated water (tritium oxide) to account for dispersion and dilution. In this method also, hellium may be applied as a biochemically inactive tracer gas. It will, however, call for the use of a mass spectrometer for measuring the hellium concentration. A modification of these methods may also involve the use of hydrocarbon tracer gas.

The oxygen transfer capacity for submerged air devices may also be estimated by an off-gas method (Redmon et al., 1983). This method appears to be very reliable under practical conditions (Boyle and Campbell, 1984).

In recent years, evaluation of many aeration devices has been made with the application of upgraded testing methods (McKinney, 1981; Rakness, 1981; Environmental Protection Agency, 1981; Doyle et al., 1983; Heduit and Racoult, 1983; etc.). Basically, most of the aeration devices are capable of producing the required aeration capacity, but, in achieving that goal, they may show different aeration economy values (see p. 3) and cause different mixing of the aeration tank contents. Placement of aeration devices and tank geometry may have an important influence on the operation of aeration (Smith et al., 1978; Sullivan, 1983; etc.) To correctly evaluate the specific air diffuser performance, Sekizawa et al. (1985) recently introduced the concept of the air diffuser performance. Values of this factor were determined from simultaneously measured concentrations of oxygen and carbon dioxide in off-gas from aeration tanks under operating conditions.

A specific problem of fine-bubble aeration is the associated alpha coefficient which, under some circumstances, may drop quite substantially (Huibregtse, 1983; Stenstrom and Hwang, 1983; etc.). The mechanical surface aerators usually show much higher alpha values.

3. OXYGENATION COSTS ANALYSIS

The oxygenation (aeration) costs in the activated sludge process are composed of:

a) the capital costs of the aeration devices and the required additional equipment such as air intake units, air filtration units, air compressors, and air distribution facilities for the compressed air systems;

b) the operational costs of aeration including the energy consumption for aeration (aeration economy) and the required personnel for normal operation of the system; and

c) the costs of maintenance of the system including the costs of repairs, cleaning, and replacements of the system elements.

The values of aeration economy (also called aeration efficiencies) quoted by equipment manufacturers may refer to the total energy requirement for aeration or may exclude energy losses not typical for the operation of oxygen transfer. The former values, which are, of course, numerically lower, are called the "gross economy" of the operation, and the latter, the "net economy". For comparative evaluation of different aeration systems, the "gross economy" values should be taken into consideration. It is not unusual to find that sometimes the real energy consumption by an activated sludge treatment plant is as much as twice as high as was originally anticipated because the aerators were tested without consideration for operational conditions or additional energy uses only indirectly associated with aeration. Some excessive claims of high efficiency of specific aeration devices are based on such assumptions.

The costs of maintenance of an aeration system may be an important component of its total costs. These costs include the cost of replacement, repair, and cleaning of the system elements. In the past, replacement of gear boxes added considerably to the costs of surface aeration. Presently, the longevity of these units is quite satisfactory (Stukenberg, 1984). For fine-bubble compressed air aeration, the cleaning of diffusers is still a serious problem. The internal clogging by dust particles is generally kept under control by efficient air filtration, but the external biological and chemical fouling creates numerous operational difficulties. The application of chemicals for phosphorus elimination contributes substantially to chemical fouling of diffusers at some locations.

Biological fouling of compressed air diffusors may occur in different degrees, from only an increase in the size of the formed air bubbles by a coating of the diffuser (coarse bubbling), to noticeable increases in air pressure head losses. Different organisms may grow on diffusers, and the growth of some of them appears to be seasonal. Some biological slimes can be easily removed from diffusers by various mild cleaning procedures, but some are more stubborn. Biological fouling (sliming) of fine-bubble diffusers is believed to be caused by a number of factors, including high food to microorganisms ratios (e.g. more fouling at the head of the aeration tanks with limited backmixing), high soluble BOD levels, low dissolved oxygen concentrations, and low mixing levels (Houck and Boon, 1981). Boyle and Redmon (1983) recently presented an interesting review of the present understanding of biological fouling of fine-bubble diffusers and indicated that biofouling is highly specific to the plant and the wastewater.

Chemical fouling may result from local water hardness, discharges of industrial effluents, and application of chemicals for phosphorus precipitation.

Diffuser cleaning may be done "in situ" or may be connected with diffuser removal from the aeration tank. Diffuser cleaning "in situ" may include internal gas injection, mechanical jetting, steaming and brushing. Experiments on an injection of hydrochloric acid, sulfur dioxide and formic acid (HCOOH) to the pressure-air system have been performed by Bretscher and Hager (1983). Periodic application of formic acid proved to be most effective and was suggested as a method to prevent diffuser-clogging. Similar results with a full-scale application of anhydrous hydrogen chloride gas at the treatment plant in Seymour, Wis., were recently reported by Vik et al., (1984).

Aeration systems consume most of the power required for activated sludge treatment, and with growing power costs, more efficient aeration may be a key factor for cost-effective wastewater treatment. Diffused-air aeration with fine-bubble diffusers is about 50% more efficient than course-bubble aeration, or use of sparger rings with submerged turbines. Good mechanical surface aerators show lower oxygenation economy for clean water tests than fine-bubble diffusers, but, under operational conditions, they may produce the same, or similar, effects because of low alpha values for fine-bubble systems. A rough generalization of several studies on the subject leads to the statement that good mechanical surface aerators are capable of producing a net economy of oxygen solubilization of 1.8 kg O_2/kWh for clean water tests, and 1.6 kg O_2/kWh for sewage tests, while the fine-bubble aerators show a net economy of 2.8 kg O_2/kWh for clean water, 2.1 kg O_2/kWh for nitrifying system, and 1.6 kg O_2/ kWh for sewage tests (Houck and Boon, 1981; Kayser, 1982; etc.). Under such circumstances, the mechanical systems could be preferred, especially for smaller plants, as they require less operational labour for maintenance of the system (diffuser cleaning).

Evaluation of diffused-air aeration by percentage of solubilized oxygen is misleading as the percent of used oxygen does not reflect the energy consumption for such solubilization e.g. oxygen utilization in a deep-shaft system may be as high as 54% (LeClair - personal communication) but its net aeration economy under operating conditions is only 1.28 kg/kWh versus 1.6 kg/kWh for fine-bubble diffusers which show utilization of oxygen in the range of 15% only.

Automatic control of aeration systems may produce substantial savings, but not all aeration devices are equally adaptable for such control. Several studies have been performed on the subject (e.g. Speirs and Stephenson, 1984; Howell et al., 1984; Johnson et al., 1984; etc.).

Except for small plants, the exchanging of existing coarse-bubble diffusers or submerged turbines for fine-bubble diffusers is definitely justified. In the case of small plants, however, the increased operational requirements associated with such a change, should be carefully analysed. Such problems were discussed recently by Stenstrom et al. (1984).

A general approach to mathematical modelling of energy consumption in biological wastewater treatment was presented by Kubota and Fujie (in press), and detailed studies on particular applications were given by Metzler (1983) and Linden (1983).

4. MIXING IN AERATION TANKS

The purpose of aeration in the activated sludge process is not only to supply oxygen for microorganisms, but also to maintain microorganisms in suspension and to mix properly the contents of the aeration reactors. Separation of these functions appears technologically attractive (Barnhart, 1983), but it is practised only in a very limited way and without much technological success.

Mixing conditions in an aeration tank can be evaluated by tracer dispersion studies, uniformity of mixed liquor suspended solids concentrations, oxygen uptake rate variations, variations in oxygen transfer determinations, and values of bottom velocities. The latter approach, which requires that a velocity of 0.25 m/s be maintained at the tank bottom to suspend activated sludge flocs, appears to be the most common and practical, although, there are still some areas of uncertainty.

There are also endeavours to estimate the mixing characteristics of surface aerators on the basis of energy input into the given aeration tank. The most frequently quoted requirements are 13-26 W/m^3 (0.5-1.0 hp/1,000 cu.ft). These values are sometimes misleading, as are the formulations about the pumping effectiveness of the surface aerators, or air flow requirements for diffused air aeration (0.02-0.03 m^3/m^3 min.).

The interrelationship between mixing characteristics and tracer response curves in aeration tanks was studied recently by Fujie et al, (1983) and Bode and Seyfried (1984). Problems with return sludge interference were successfully eliminated. This approach, however, does not appear to relate well enough to the homogenity of the aeration tank.

Mixing in the compressed-air aeration systems has been studied by Harremoes (1979) who characterised the velocity of the formed plume. These findings were also confirmed by Roustan et al., (1984) who indicated that the aeration tank bottom velocity depended on activated sludge contents in the tank and should be several times higher than the settling velocity of activated sludge. The spacing of the air-diffusers appears to be an important factor in preventing "dead zones" in aeration tanks and effectively utilizing the capacity of the system (Gilbert and Sullivan, 1983; Khudenko and Shpirt, 1983, etc.).

Basically, the application of mechanical aerators creates many more mixing problems in the aeration tanks than does compressed air aeration. Some stratification of mixed liquor suspended solids concentration has been observed in both relatively shallow oxidation ditches and deep tanks aerated with large surface aerators. Usually these mixing problems can be eliminated by the introduction of proper baffles and proper placing of aeration devices. Goldstein (1979) evaluated hydraulic losses in aeration tanks with horizontal rotors due to baffles and guiding walls for circulating the mixed liquor. The calculated head lift per rotor proved to be in the range of 0.5-1.5 cm., and the pumping efficiency of rotors proved to be low. Khudenko (1983) described a development of self-propelled aerators, and Nestman (1983) studied the optimization of mechanical aerators in an hydraulic two-phase flow model.

5. STRIPPING, AEROSOL FORMATION AND COOLING ABILITIES

Several odorous substances are present in wastewater or can be formed by decomposition of some substances present in wastewater. The odorous substances may be stripped from wastewater and released into the atmosphere during aeration. Similarly, bacterial aerosols may be formed by the operation of aeration devices, and this operation may cause less or more effective cooling of the mixed liquor.

As a rule, the mechanical surface aerators are more efficient systems for stripping, aerosol formation, and cooling of the mixed liquor than fine-bubble compressed air aeration. Therefore, for a given type of wastewater, use of surface aeration produces more odour problems, aerosol formation problems, and mixed liquor cooling problems than an application of fine-bubble air aeration. Even less of these problems may be expected with oxygen-supported aeration and use of commercial oxygen only. The preference sequence of aeration systems from this angle would reflect the above regularity.

Mass transfer mechanism of volatile substances by aeration was the subject of several studies (Matter-Mueller et al., 1981; Pellizari, 1982; Chrostowski et al., 1982; Roberts and Dandliker, 1982; Ball et al., 1984; Roberts et al., 1984; etc. Lurker et al. (1982) indicated that activated sludge aeration tanks were a major source of airborne release of organic compounds, and that aeration rate and suspended solids concentrations appeared to influence the rate of release. In a follow-up study, Lurker et al. (1984) investigated more closely the controlling factors influencing the atmospheric release of chloroform and chlorobicycloheptadiene from simulated wastewater treated by the activated sludge process. The stripping followed first order kinetics. The aeration rate was the only significant variable influencing the release of chloroform, but the release of chlorobicycloheptadiene was also influenced by mixed liquor suspended solids concentrations and the presence of detergent in the system. These results suggest that chloroform was stripped from a dissolved state, and chlorobicycloheptadiene from an adsorbed state.

Stripping from aeration tanks, in some circumstances, may be beneficial. For instance, it may control the removal of carbon dioxide from nitrifying systems, which otherwise might show some excessive decreases in pH.

Emission of odours from a wastewater treatment plant may be limited by the better utilization of air, introduced both by a diffused-air system or surface mechanical devices. Schlegel (1979) suggested an application of partial covers on diffused-air aeration tanks, and the additional use of commercial oxygen at the head of tanks with limited backmixing. Engelhardt et al. (1980) and Malle (1981) successfully used plastic covers over large Carrousel aerators and the surrounding water surface.

Aerosols generated by open aeration systems are carriers of bacteria and have the potential to cause several health problems. According to Wanner (1979), fine-bubble aeration generates the least aerosols; somewhat larger aerosol generation is caused by medium-size bubble aeration, and many times larger aerosol generations was observed at various surface aeration systems. However, the spray systems used for foam control contribute substantially to the formation of bacterial aerosols. In aeration systems directly exposed to the atmosphere, the presence of an increased bacteria concentration in the ambient air is observed up to a distance of 200 m. Respective health hazards have not been well documented. However, for the aeration systems which are housed, they are quite serious (Wanner, 1979).

The Health Effects Research Laboratory of the U.S. Environmental Agency arranged for several epidemiological studies to gather information on health effects associated with aerosols from uncovered wastewater treatment plants. The results of these studies were presented at a Symposium held on September 19-21, 1979 (Pahren and Jakubowski, 1980), and certainly have enriched the knowledge on the subject. Although no general conclusions were formulated at that time, it was clearly stated that a potential existed for plant workers and nearby residents to inhale viable organisms.

For surface aeration systems, aerosol generation can be controlled by the use of substantially enlarged bridges or hoods, both for horizontal and vertical mechanical aerators, and by an application of "skirts" hanging on the sides of the bridges. The costs of these control steps should be added to the total costs of the whole aeration system.

Cooling effects of aeration systems are a function of several parameters of the operation. Ford et al. (1972) recognized that mechanically-aerated aeration tanks are also cooling ponds, and predicted the temperature in such systems by the calculation of heat loss attributable to the aeration spray and through the surface. The spray heat loss was calculated from the differential enthalpy of the air flow through the spray cloud. For this purpose, the cross-sectional area of the spray pattern exposed to the air flow should be known, the velocity of air through the spray should be estimated, and the exit air humidity and temperature predicted. The surface heat losses can be estimated on the basis of relative air humidity, wind velocity, air temperature, solar radiation and mixed liquor temperature.

6. NOISE GENERATION

High noise levels may have an adverse effect on human health, may be annoying and irritating, and may even disturb some particular activities. Usually noise generation is associated with mechanical aeration, although compressed air blowers, and oxygen generation units may also be substantial sources of noise.

Noise generation in the surface aeration systems is composed of noise created by the specific water movements (splash) and noise from the operation of gearboxes and motors. If required, the latter sources of noise may be substantially decreased by proper device design and proper noise insulation. In the case of compressed-air aeration, silencers should be provided on both the intake and discharge side of the blowers.

Noise generation by sewage treatment plants was the subject of a general study by Saelzer and Freimuth (1978). A detailed analysis of noise generation by horizontal mechanical aerators was presented by Werner (1984). He also discussed the required preventive measures.

7. COMPARISON OF AERATION SYSTEMS

Aeration systems, generally, can be divided into mechanical and diffused air systems. More detailed systematics are presented in TABLE 7-1. In practical applications, good low-speed surface aerators are completely comparable with fine-bubble diffusers in

Table 7-1

CHARACTERISTICS OF AERATION SYSTEMS

AERATION SYSTEMS	BASIC CHARACTERISTICS
1. MECHANICAL AERATORS WITH HORIZONTAL AXES	
1.1 Aeration brushes and cages	good oxygenation capacity and economy, mixing problems in some types of aeration tanks, high but controllable stripping, aerosol formation and cooling abilities, controllable noise generation
1.2 Aeration discs	questionable oxygenation capacity and limited experience with the system; this system requires construction of special and relatively expensive aeration tanks
2. MECHANICAL AERATORS WITH VERTICAL AXES	
2.1 Low-speed surface aerators	basic system of mechanical aeration in the activated sludge process, characteristics like 1.1
2.2 High-speed surface aerators	more applicable for aerated lagoons than for activated sludge aeration tanks, excessive turbulence is formed in the direct vicinity of the aeration unit
3. DIFFUSED-AIR AERATORS	
3.1 Fine-bubble diffusers	basic system for compressed air aeration in the activated sludge process, good oxygenation capacity, energy consumption, and usually satisfactory mixing in aeration tanks, limited stripping, aerosol formation and cooling, possibly negligible noise generation, problems limited to biological and chemical fouling of the diffusers and a low alpha coefficient
3.2 Medium-size bubble diffusers	generally poorer oxygenation economy than 3.1, but less problems with diffuser fouling, more effective stripping and aerosol formation
3.3 Coarse-bubble diffusers	obsolete system; poor oxygenation capacity and oxygenation economy
4. COMMERCIAL OXYGEN AERATION	may be used in association with mechanical or diffuser units; its oxygenation capacity is excellent but economy depends on the process requirements; insufficient CO_2 stripping may create some problems
5. COMBINED AERATION SYSTEMS	
5.1 Submerged turbines	in current engineering designs it is an obsolete system not capable of providing satisfactory oxygenation capacity and economy
5.2 Rotating biological discs in aeration tanks	relatively new approach, only limited information on the subject is available
5.3 Static tubes and various jet aerators	systems applicable only for special designs of aeration tanks
5.4 Diffused-air aeration with a forced horizontal flow	undocumented, excessive claims on oxygenation capacity and economy of such systems have been presented; technically they show a reasonable similarity to systems 3.2
5.5 Down-flow draft tubes for diffused air or oxygen	relatively new approach, only limted information on the subject is available
6. AERATION IN BIOLOGICAL FILTERS	in current engineering designs such systems do not show attractive characteristics very little specific information is available
7. USE OF CHEMICAL OXYGEN	applicable only for some special industrial wastewaters and in pre-denitrification stage of some treatment systems

terms of achievable oxygenation capacity of mixed liquor and respective energy consumptions. However, the use of surface aerators may create some correctable problems with the aeration tank hydraulics, and will show more stripping which may be beneficial or not. Also aerosol formation will be more intensive under these conditions as will the cooling of mixed liquor. The latter may be a sensitive point under some climatic conditions. The noise generation by surface aerators will be much more intensive than with compressed-air systems. On the other hand, the weak points in fine-bubble diffuser aeration are the diffuser-fouling phenomena which may require frequent replacement and cleaning of the diffusers. These operations are expensive in terms of labour and may seriously affect the total economy of the system.

8. CHECKLIST FOR SELECTION

The selection process for aeration devices for a specific activated sludge treatment facility is a multi-stage exercise, including:

a) analysis of the selection restrictions due to local factors and factors arising from the design;
b) equipment pre-selection on the basis of energy considerations:
c) detailed analysis of the technological factors involved in the operation of the aeration devices considered (oxygenation capacity, oxygenation economy and mixing performance);
d) detailed analysis of environmental factors (gas stripping, aerosol formation, cooling, and noise generation); and
e) final comprehensive cost analysis of acceptable aeration systems, comprising elements added to correct or improve the technological and environmental performance of the devices.

Each stage of the selection process will alter the preferences among the available devices and will shorten the list, but the last stage will bring the final recommendations (Fig. 1).

There are several local factors and factors arising from the specific design features of the activated sludge treatment plant which may have a decisive influence on the selection of aeration devices and may overrule or substantially change the

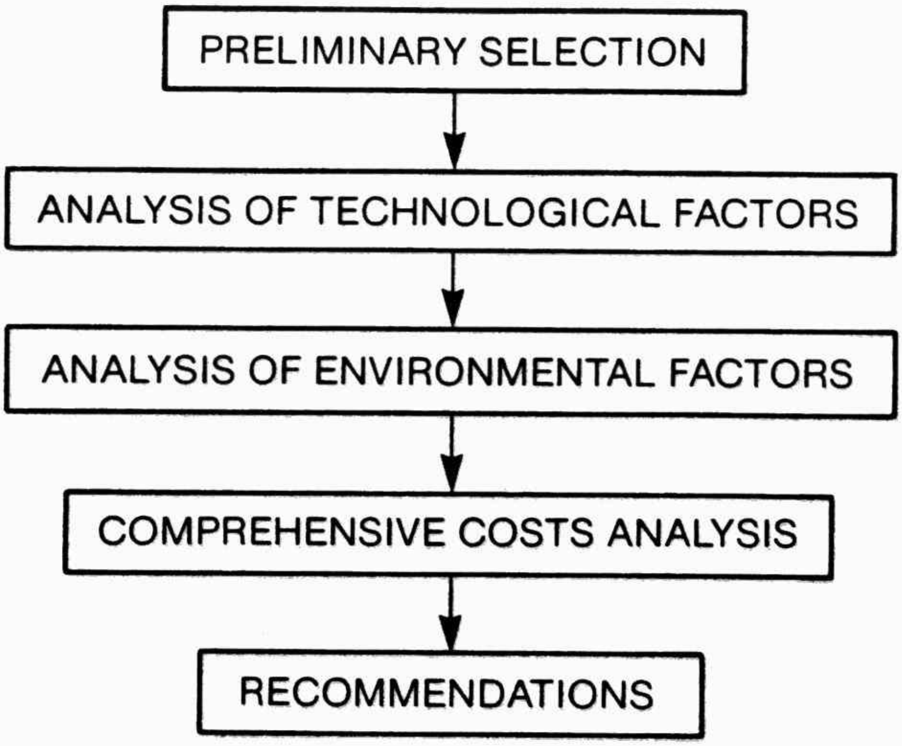
PRELIMINARY SELECTION
ANALYSIS OF TECHNOLOGICAL FACTORS
ANALYSIS OF ENVIRONMENTAL FACTORS
COMPREHENSIVE COSTS ANALYSIS
RECOMMENDATIONS

Fig. 1. Action Chart for Aerator Selection

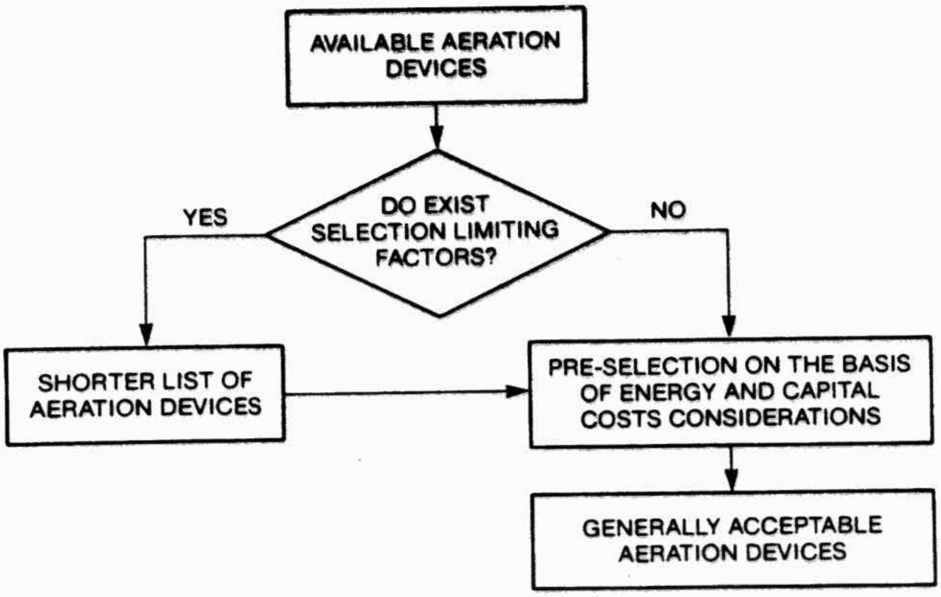
AVAILABLE AERATION DEVICES
DO EXIST SELECTION LIMITING FACTORS?
YES
NO
SHORTER LIST OF AERATION DEVICES
PRE-SELECTION ON THE BASIS OF ENERGY AND CAPITAL COSTS CONSIDERATIONS
GENERALLY ACCEPTABLE AERATION DEVICES

Fig. 2. Preliminary Selection of Aeration Devices

conclusions derived from a logical analysis of technological and environmental parameters of the operation (Fig. 2). These factors include especially:

- the size of the installation and the availability of operational personnel (for small plants, simplicity of operation may be very important);
- the plant loading characteristics (for example, those required to maintain adequate mixing in the aeration tanks at periodically-decreased aeration capacities);
- the depth of the aeration tanks (deep tanks due to limited availability of land, and shallow tanks due to high groundwater levels), etc.

Equipment pre-selection on the basis of energy considerations is becoming a more and more important selection step in view of increasing energy costs, and even more serious predictions in this respect. Some aeration devices should be excluded from the decision analysis on this basis, especially if they do not offer any special operational simplicity or, if such simplicity is not considered important for a given application. This pre-selection will not take the place of a more detailed cost analysis when considering the technological parameters, but will restrict this analysis to devices which are more promising.

The analysis of technological and environmental factors in the selection process is shown in Fig. 3 and Fig. 4. A summary of this analysis is presented in the form of the following checklist:

1. Check whether the expected oxygenation capacity of the aerator has been tested:
    (a) in the testing tank of a size similar to the units of the designed facility,
    (b) under operational conditions, and
    (c) for mixed liquor containing characteristic components of wastewater which will be treated in the designed facility.
2. Check whether the energy consumption claimed for the aeration process is presented in terms of total energy requirements (gross economy or gross efficiency) for the conditions reflecting the testing of the oxygenation capacity.

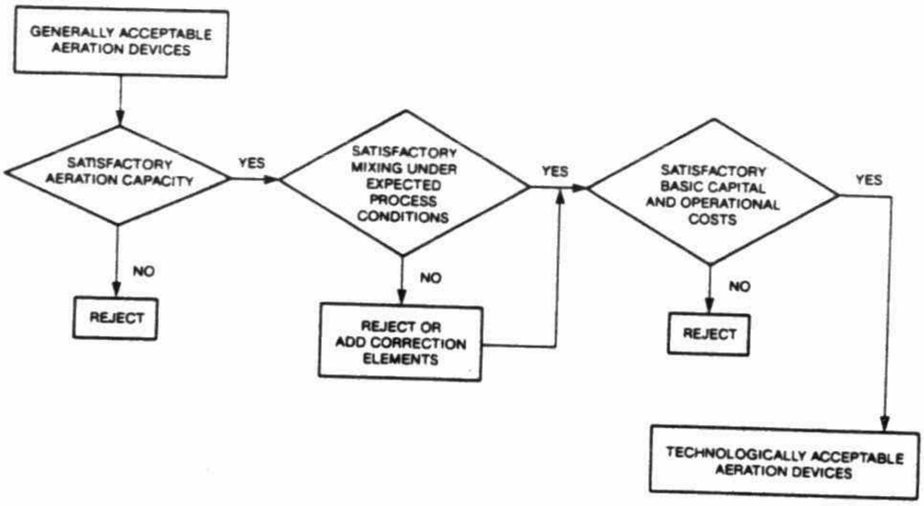
GENERALLY ACCEPTABLE AERATION DEVICES
SATISFACTORY AERATION CAPACITY
YES
NO
REJECT
SATISFACTORY MIXING UNDER EXPECTED PROCESS CONDITIONS
YES
NO
REJECT OR ADD CORRECTION ELEMENTS
SATISFACTORY BASIC CAPITAL AND OPERATIONAL COSTS
YES
NO
REJECT
TECHNOLOGICALLY ACCEPTABLE AERATION DEVICES

Fig. 3. Analysis of Technological Factors

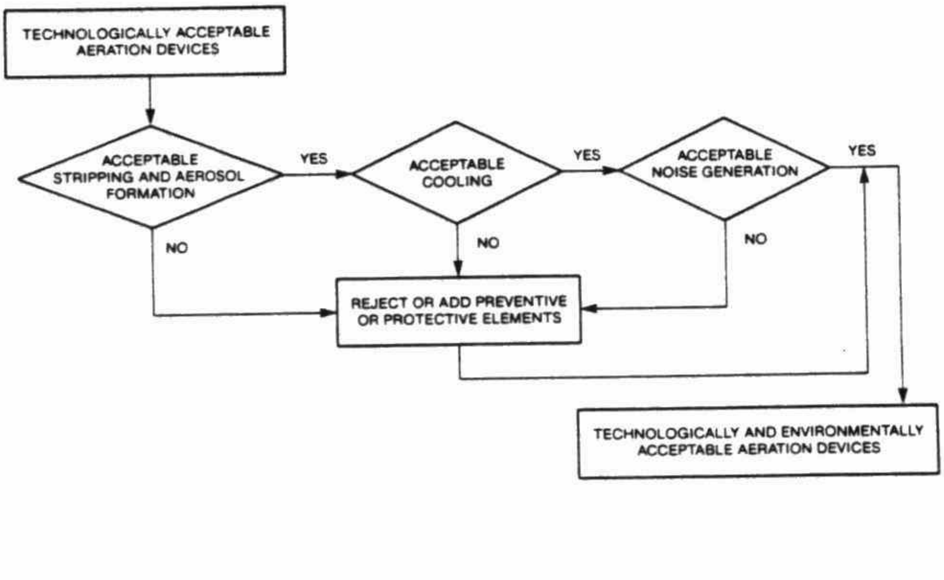
TECHNOLOGICALLY ACCEPTABLE AERATION DEVICES
ACCEPTABLE STRIPPING AND AEROSOL FORMATION
YES
NO
ACCEPTABLE COOLING
YES
NO
ACCEPTABLE NOISE GENERATION
YES
NO
REJECT OR ADD PREVENTIVE OR PROTECTIVE ELEMENTS
TECHNOLOGICALLY AND ENVIRONMENTALLY ACCEPTABLE AERATION DEVICES

Fig. 4. Analysis of Environmental Factors

3. Check requirements and expectations regarding replacement, repairs, and cleaning of the aeration system elements. Fine-bubble diffusers are especially susceptible to biological and chemical fouling and have to be cleaned or replaced quite often under some circumstances.
4. Examine thoroughly the information available on the mixing characteristics of aerators submitted for selection. Special care is required with surface aerators expected to operate in tanks of somewhat unusual size or shape. If there are any doubts, inspection of similar facilities may be advisable.
5. For surface aerators, stripping of some mixed liquor components may be too intensive but, for some fine-bubble compressed air aeration systems, it may not be sufficient. Therefore, the possibility of air pollution from the use of surface aerators should be looked into, and insufficient removal of carbon dioxide, e.g. from the deep tanks for the nitrification zone of the activated sludge process, aerated with fine-bubble diffusers, should be investigated.
6. Intensive aerosol formation in new aeration units is almost entirely limited to the use of mechanical surface aerators, as high-flow compressed-air aeration, as in the INKA system or with coarse-bubble diffusers, is less common at present. In cases where aerosol formation may create some problems, preventive steps such as the use of enough large bridges over the aerators and/or some plastic skirts on the bridge sides, should be taken. For economical comparisons, the cost of these modifications should be incorporated into the costs of the aeration system.
7. Effective cooling of mixed liquor is associated with the operation of surface aerators. The units themselves should be protected against icing. Check whether cooling of mixed liquor is an important issue, for surface aerators should not be used in such cases.
8. Noise generation is also associated with surface aeration. It can be limited by the application of proper noise insulation to motors and gear boxes. Check whether noise may be a problem

and how much it will cost to control it.

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COMPOSITION, MINERALOGY, AND MORPHOLOGICAL NATURE OF INDUSTRIAL WASTES AND THEIR LEACHIBILITY

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Key words: Industrial Waste, Leachibility, Waste Stabilization, X-ray Analysis, Electron Microscopy.

ABSTRACT

The composition and nature of a solid waste must be known in order to predict the leachibility (stabilization) of the waste under a variety of environmental conditions. Whereas the more traditional leach test reveals the mobility of a substance under only the testing conditions, knowledge of the binding of the metal to the solid substrate permits the calculation (and confirmation by testing) of metal mobility under any postulated environment. In addition, knowledge of other solid material may be important to the reactivity of the waste by setting up various chemical buffers, impeding permeation, etc.

This research, in its initial stages, considers the characterization of industrial waste (in order) from its composition, the chemical partial extraction of certain metals, its mineralogy, its morphology, and the specific association of metal to substrate at the micrometer scale. The overall major and minor element composition is obtained by X-ray fluorescence and instrumental Neutron Activation Analyses. In addition, loss on ignition, total sulfur, and organic/inorganic carbon are analyzed. The sequential extraction follows that of Tessier et al, and operationally defines the metal concentrations associated with ion exchangeable, carbonate, Fe/Mn oxides, organic, and residual phases. X-ray diffraction analysis is used for major elemental analysis to reconstruct the crystalline compounds. Both Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) are used to morphologically characterize the waste as to size and crystallinity, and to confirm the mineralogy and association of metal and solid. Computer-aided elemental mapping of images with respect to mineralogy further confirms the association of metal and solid substrate. Other follow-up measurements include surface area by the BET technique.

An industrial foundry waste, a plating waste, and a coal waste are used as examples to illustrate the above techniques and the strengths and weaknesses of each procedure. Then some proposals for stabilizing the wastes are developed using the accumulated information on the metal-substrate associations.

COMPOSITION, MINERALOGY AND MORPHOLOGICAL NATURE OF INDUSTRIAL WASTES AND THEIR LEACHABILITY

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Abstract: Determinations are carried out in order to better define the nature of binding of potentially toxic trace metals in industrial wastes. These determinations include bulk chemistry, individual particle chemistry, X-ray diffraction analysis, electron microscopy, and selective sequential extraction. Information from each determination is compared. Results of these analyses can be used to predict mobility of metals under different environmental conditions.

INTRODUCTION

This paper is concerned with the mobilization of potentially toxic trace metals in industrial wastes. Whereas most studies concentrate upon column or batch leachability [1], the approach taken here is to characterize the nature of the waste itself, and from the resulting information, predict the leachability of the waste under various environmental scenarios. Information on the nature of the waste can also be used to specify more sensitive leaching tests.

This study describes the methodology for characterization of the waste. It is part of a continuing project whose goal is to predict mobilization of metals in wastes under various environmental conditions, given details on the nature of the waste.

The approach used is to design a series of analyses of the wastes so as to be able to specify the nature of and binding energy of trace metals (TM). The binding energy of TMs may vary widely, being weakly sorbed onto substrates and hence very mobile or incorporated into the crystalline lattice of a very stable substance, hence being immobile except for extreme chemical conditions. Depending upon the nature of the substrate and the binding of the TM, the TM may be quite mobile/immobile under acid/base, oxidizing/reducing, and varying solute chemistry [2]. Therefore there is no one general "leaching test" that can accurately predict the mobility or immobility of a TM without prior information regarding the waste and the disposal environment itself [3].

TMs may also occur within a specific waste in more than one coordination. For example, one may determine that a proportion of a TM is held as a very weak sorbed complex, whereas another proportion may be strongly bound in an insoluble crystalline material. Therefore bulk chemical analyses give incomplete information as to the concentration of mobile TMs.

Darcel [4], in a literature review of waste stabilization notes that the key factors in most mobilization studies are the pH, the redox condition, the extraction method, substrate surface area and solid/liquid ratio.

Waste substrates themselves are reactive, and they may serve as pH buffers, redox buffers, or sites for adsorption and reaction with TMs. It is therefore not surprising that the actual groundwater quality at waste sites bears little relationship to test leachate chemistry [5]. Fundamental characterization of the TMs and the waste solids provides information that can be used to better predict the nature of reactions that go on under natural conditions.

METHODS OF ANALYSIS

The following scheme of analysis considers 1) the overall bulk chemistry, 2) the crystalline components, 3) the morphology of the waste, 4) elemental associations at the micro-meter scale, and 5) the extractability of selected TMs under various chemical conditions. Results from these five techniques are compared for consistency of results. Thus the results of all five analytical methods must be compatible before a waste is considered characterized. For example, the bulk chemistry is correlated to the extent possible with X-ray diffraction analysis of crystalline substances. Individual morphological and elemental analyses [from computer-aided energy dispersive analysis (EDS) on an electron microscope (SEM)] are related to X-ray diffraction analysis and bulk chemistry. The extractibility of TMs under various conditions is related to the solubility of defined solids and the sorption characteristics of the defined solids. The above characterization studies are carried out on end-member samples when solubility and compositional analyses are not available.

The following summarizes the various methods of analysis:

1) Bulk chemistry: The major elements are determined by X-ray fluorescence (XRF) analysis on a pellet fused with lithium metaborate. Trace metals are determined on a pressed pellet containing high purity carbon as a matrix. Adjustment for background and matrix interference is carried out automatically. Calibration curves are developed from standard reference material.

Trace elements are also analyzed by instrumental neutron activation analysis (INAA) and by atomic absorption spectroscopy (AAS). Both short and long-lived isotopic analysis, using thermal and epithermal radiations respectively, were carried out. Counting of gamma rays was carried out on a Canberra S-90 multi-channel analyser using a 22% efficient detector. Both the INAA and XRF spectra are scanned for abundant TMs in addition to those specified. The sum of the concentrations of the 5 AAS analyses (see below)is compared to XRF and INAA results.

2) X-ray diffraction analysis: Powder diffraction analysis is normally carried out using copper radiation and scanning from about 6-70° 2θ. The XRD peaks are compared to standard references for identification of crystalline substances. The composition of the defined solids is in turn compared to bulk chemistry.

3) Electron microscopic analysis: Powder samples were mounted on double-sided adhesive tape and transferred to an SEM (stub) holder. Samples were carbon-coated (Edwards carbon evaporator). Fine particle samples (e.g. nos A, C, D below) were mounted on nickel or copper carbonized formvar coated EM grids from a water suspension of sample and transferring to the grid with an Eppendorf pipette with oven drying at 40°C. Particle analysis is carried out using an ISI DS 130 scanning-transmission electron microscope. Examination is first carried out for morphology at low (2000X) and high magnification (20-30,000X) in the SEM/TEM mode.

Individual areas (particles) of about 0.5 uM square are analyzed for elements using a Princeton X-ray analyzer (GAMMA TECH 4) at 15 kV and collection for 40 s. Quantitative analysis of individual particles are obtained after correction for dead time, background and atomic number, correction for matrix effects, and by calibration with particles of known composition. The detection limit for this set-up is about 0.5%. The accuracy relative to reference samples is 5% for SiO_2 and 2-3% for Al_2O_3, Fe_2O_3, Cao, MgO, K_2O and Na_2O. Similar accuracies are provisionally estimated for Cu, Cr, Ni, Pb and Zn. At present, matrix corrections are known for common elements. Elemental analysis now is well-proven for common elements, and work is continuing on elemental analysis when TMs occur at elevated concentrations.

4) Sequential extraction analysis: Sequential extractions of wastes are carried out according to the Tessier method [6]. The five extractions in sequence are:

a) Exchangeable: a 1 gram (normalized to dry weight) sample is extracted at room temperature for 1 hr with 8 mL of M $MgCl_2$ at pH of 7 and continuous agitation on a wrist shaker. The sample is then centrifuged for 40 min, and the supernatant is removed for analysis of TMs by AAS using standard addition technique. (The sample residue is washed with a small volume of high purity water, and the sample is concentrated by centrifugation and decantation between each step.)

b) "Carbonate bound": 8 mL of M NaOAc, adjusted to a pH of 5 with acetic acid, is added to the residue from a). The samples are agitated for 5 hrs at room temperature, centrifuged, and the supernatant is removed for analysis of TMs. The residue to washed as in a).

c) "Bound to Fe-Mn oxides": The residue from b) is extracted for 6 hrs with 20 mL of 0.04 M NH_2OH-HCl in 25%(v/v) HOAc at 96°C with occasional agitation.

d) "Bound to organic matter": 3 mL of 0.02 M HNO_3 and 5 mL of 30% H_2O_2, adjusted to a pH of 2 with HNO_3, is added to the residue from c). The mixture is heated for two hours in an oven at 85°C with occasional agitation. Then another 3 mL of 30% H_2O_2 (pH of 2) is added, the sample is heated at 85°C for an additional 3 hrs with occasional agitation. The sample is then cooled, and 5 mL of 3.2 M

NH_4OAc in 20% (v/v) HNO_3 is added, the sample is diluted to 20 mL and agitated for 30 min. The sample is then centrifuged, and the supernatant is extracted for analysis of TMs. The residue is washed as in a).

e) "Residual": The residue from d) is digested with 10 mL of aqua regia for 2 hours. The digested sample is washed through a 0.45 uM filter paper and analyzed for TMs.

For AAS analysis, the supernatant from steps a) - d) is acidified with 3 drops of ultra-pure HNO_3 and diluted to 35 mL. Step e) normally requires a dilution of 50-100X. Two standard additions are made to a 10 mL aliquot of sample. Some samples high in TMs required further dilution of 10-30X so that a total dilution of about 1000X may result. Dilutions were made gravimetrically.

RESULTS OF ANALYSES ON SELECTED INDUSTRIAL WASTES

Five industrial waste samples were obtained from the Ontario M.O.E. for characterization. These samples were:
a) a smelter dust, b) a coal fly ash, c) steel flue dust, d) an iron foundry dust, and e) a plating sludge. All but sample e) were in a near dry state; sample e) contained 67% H_2O upon receipt, and furthermore, the sample was quite heterogeneous in composition. Therefore a large sub-sample was dried and well-mixed in order to ensure homogeneity.

Table 1 gives the results for the bulk chemistry of the five samples. A summary of the bulk analysis for the five samples is:

a) smelter dust: a high iron-oxy-hydroxide (e.g. LOI) substrate with about 4.5 % Cu, 3.0% Ni and elevated (300-1000 mg/kg) Cr, Pb and Zn. It is probable that some of the TMs exist as sulfides (8.4% S).

b) coal fly ash: Ca-Al-Fe-Si oxy-hydroxides, some S compounds and C. TMs are at the low 100s mg/kg.

c) steel flue dust: Fe-Mn oxy-hydroxides with lesser Al and Si. Elevated Pb (3.5%) and Zn (15%) probably associated with Fe/Mn oxy-hydroxides or as simple oxides. Cd, Cu and Cr occur at elevated levels in the 100-3000 mg/kg range.

TABLE 1. Bulk chemistry of five industrial waste samples from XRF, INAA and AAS analyses. All analyses are for dry weight. LOI - loss on ignition at 1000°C compared to 100°C dry weight.

	(a) Smelter dust			(b) Coal fly ash			(c) Steel flue dust		
	%			%			%		
	INAA	AAS	XRF	INAA	AAS	XRF	INAA	AAS	XRF
SiO_2			9.4			34.0			2.1
Al_2O_3	2.5		1.2	18.1		19.8	0.49		0.23
Fe_2O_3	68.2		67.8	26.3		21.5	68.6		61.9
MgO			1.2			0.7			1.4
CaO			1.1			3.2			5.6
Na_2O			<0.3			<0.2			1.5
K_2O			0.2			<0.2			0.8
TiO_2	0.18		0.3	0.68		1.1	0.55		0.03
MnO	0.05	0.18	0.1	0.05	0.03	0.07	5.1	4.5	4.8
P_2O_5			0.03			0.10			0.07
Cl	0.01			<0.02			2.26		
S			8.4			1.3			0.5
C			0.2			10.5			0.8
LOI			13.6			14.2			6.5
	mg/kg			mg/kg			mg/kg		
Cu	47400	42000	37000	<36	89	116	2060	7090	1860
Cr	340	416	370	176	1680	430	4000	NA	3200
Cd		55			26			532	
Ni	35000	24000	28000	98	190	98	323	1324	148
Pb		1490	660		218	63		34000	35000
Zn		2040	1030		77	128		153000	150000

	d) Iron foundry dust			e) Plating sludge		
	%			%		
	INAA	AAS	XRF	INAA	AAS	XRF
SiO_2			18.0			4.0
Al_2O_3	2.3		1.5	1.9		2.0
Fe_2O_3	14.0		10.8	1.1		1.3
MgO			0.9			0.7
CaO			0.9			6.3
Na_2O			1.5			<0.1
K_2O			1.0			0.5
TiO_2	0.2		0.1	0.3		0.4
MnO	5.3	4.6	4.8	0.01	0.02	0.07
P_2O_5			0.1			0.1
Cl	1.1			0.08		
S			2.0			10.1
C			12.6			3.6
LOI			23.0			27.1
	mg/kg			mg/kg		
Cu	1960	8160	2180	57000	87000	98000
Cr	243	940	140	94000		114000
Cd		530			32	
Ni	100	450	120	22600	46000	57000
Pb		127000	130000		16	80
Zn		57000	60000		204	320

d) iron foundry dust: Na-K-Ca-Mg Fe/Mn-Si oxy-hydroxides with about 13% Pb and 6% Zn. Cd, Cu, Cr and Ni occur as elevated TMs in the 100-2000 mg/kg range.

e) plating sludge: Ca- carbonate/sulfate hydrated salts with about 10+% Cu, 8% Cr, and 4+% Ni probably occurring as carbonate, sulfate and hydrated salts. There may be major unidentified constituents since the analysis totals about 83%.

XRD RESULTS:

The d-spacing data from the powder diffraction analysis was compared to reflections for reference crystalline material. Major crystalline substances were determined by the occurrence of more than one major reflection characteristic of the substance and with a composition compatible with the bulk analysis. Results of this analysis are summarized in table 2. The following points out some of the more important aspects of this analysis:

a)Smelter dust: The crystalline materials are mostly magnetite, chlorite, quartz and lesser hematite. The Cu and Ni minerals are stable sulfides and more soluble oxides.

b)Coal fly ash: consists mostly of hydrated and dehydrated alumino-silicates, quartz and a hydrated calcium alumino-silicate. There is also graphite, pyrite and gypsum present. The calcium alumino-silicate would probably hydrolize to give a very basic solution.

c)Steel flue dust: is mostly magnetite with lesser hematite. The Pb and Zn minerals are present as rather stable ferrites and silicates and possibly as metals. There also appears to be a quite soluble Mn hydroxy chloride. The Ca-containing substance has not been identified.

d)Iron foundry dust: is mostly quartz, magnetite, pyrolusite and lesser hematite. The large amount of carbon appears to be amorphous to XRD. The Pb and Zn are present as rather stable ferrites and silicates and less stable manganate.

e) Plating sludge: consists of quite soluble hydroxy-carbonate-sulfate salts of Cu and Ni; the Cr salt has not been characterized yet. Lime is also present which would give a basic solution upon hydrolysis. These salts should be mobile under most conditions.

Table 2. Probable crystalline substances determined by X-ray diffraction analysis. Reflections in **bold type** reflect major intensities found; underlined values reflect weaker intensities found.

(Name, composition)	(d-spacing in decreasing intensity)					
a) Smelter dust:						
Magnetite(Fe_3O_4)	**2.53**	**1.49**	**2.97**	**1.62**	**2.10**	
Hematite (Fe_2O_3)	2.70	**2.50**	**1.70**	3.69	1.49	
Chlorite(Mg-Fe-Al-O-OH silicate)	**4.77**	14.0	7.14			
Yugawaralite($CaAl_2Si_8O_{16}.4H_2O$)	5.82	**4.68**	**3.06**			
Pyrite(FeS_2)	**1.63**	2.71	2.43	1.92	**1.45**	
Tenorite(CuO)	**2.52**	2.32	**2.53**	1.51		
Bunsensite (NiO)	**2.09**	2.41	**1.48**			
Villamaninite($[Cu,Fe,Ni]S_2$?	2.85	**1.72**	2.55			
Violarite($[Ni,Fe]_3S_4$) ?	5.82	**4.68**	**3.06**			

Other possibilities in small amounts are: silicates- actinolite, biotite, forsterite, phlogopite, quartz; TMs-chalcopyrite(Cu,FeS_2) covellite(CuS), cuprite(CuO)

b) Coal fly ash:						
Hydrated Ca-silicates	2.95	4.35	9.5			
	1.69	5.44	3.04			
Dickite($Al_2Si_2O_5(OH)_4$)	7.15	3.58	2.33	**2.51**		
Graphite(C)	**3.36**	2.0	1.67			
Gypsum($CaSO_4.2H_2O$)	**2.56**	3.06	**4.27**	**2.68**	2.87	3.79
Halloysite($Al_2Si_2O_5(OH)_4$)	7.50	3.63	4.42	**2.56**	1.68	
Hematite (Fe_2O_3)	**2.70**	**2.52**	1.70	3.69	1.49	
Magnetite (Fe_3O_4)	**2.53**	1.49	2.97	1.62	2.10	
Mullite($Al_6Si_2O_{13}$)	**3.39**	3.43	2.21			
Nontronite($NaFe_2Si_4O_{10}(OH)_2$)	13.3	4.51	3.49			
Pyrite(FeS_2)	1.63	2.71	2.43			
Quartz (SiO_2)	**3.34**	**4.26**	1.82			
Sillimanite ($Al_6Si_2O_{13}$)	**3.36**	**2.20**	**3.41**			
c) Steel flue dust:						
Beta Mn Fe	**2.09**	1.99	1.90			
Epsilon Zn Fe	**2.11**	2.58	1.90			
Franklinite ($ZnFe_2O_4$)	**2.52**	**2.98**	**1.48**			
Galena (PbS)	**2.97**	3.43	2.10			
Hematite (Fe_2O_3)	2.70	**2.52**	**1.70**	3.69	1.49	
Kempite($Mn_2(OH)_3Cl$)	**5.70**	**5.36**	2.39	**1.69**	**2.97**	
Larsenite ($PbZnSiO_4$)	**3.19**	2.85	1.49			
Lead (Pb)	2.86	2.48	1.49			
Litharge (PbO)	**3.12**	**2.81**	1.87	**1.68**	2.51	
Magnetite (Fe_3O_4)	**2.53**	**1.49**	**2.97**	1.62	**2.10**	
Plumboferrite ($PbFe_4O_7$)	2.64	**2.81**	**2.96**	3.90	**1.68**	
Zincite (ZnO)	**2.48**	2.82	2.60			

Table 2, continued

(Name, composition)	(d-spacing in decreasing intensity)				
d) Iron foundry dust:					
Bustamite $(Ca,Mn)_3Si_3O_9$	**2.24**	**3.72**	**3.23**	2.64	
Coronadite ($PbMn_7O_{14}$)	3.10	3.47	1.54		
Franklinite ($ZnFe_2O_4$)	**2.54**	**2.98**	**1.49**		
Hematite (Fe_2O_3)	2.70	**2.52**	1.70	3.69	1.49
Larsenite (Pb,Zn SiO_4)	**3.19**	2.85	4.88		
Magnetite (Fe_3O_4)	**2.53**	**1.49**	**2.97**	1.62	2.10
Massicot (PbO)	**3.07**	**2.95**	2.74	1.85	1.64
Plumbo-ferrite ($PbFe_4O_7$)	**2.64**	2.81	**2.96**	3.90	1.68
Pyrolusite (MnO_2)	**3.11**	**2.41**	1.62		
Quartz (SiO_2)	**3.34**	4.26	**1.82**		
e) Plating sludge:					
Chalcocyanite ($CuSO_4$)	**3.55**	**2.61**	**4.19**		
$Cu(OH)_2$	**3.75**	**2.64**	2.26		
Kainite ($KMg(SO_4)_2(OH)_6.3H_2O$)	**7.37**	3.08	7.77	8.12	3.03
Lime (CaO)	**2.41**	1.70	2.78	1.45	
Morenosite ($NiSO_4.7H_2O$)	**4.20**	5.30	2.85	3.45	**2.65**
Nakauriite($Cu_8(SO_4)(CO_3)(OH)_6.48H_2O$)	**2.37**	**7.31**	3.65	1.91	
$Ni(OH)_2$	4.53	**2.32**	**2.68**		

ELECTRON MICROSCOPE RESULTS:

X-ray energy dispersive spectra were gathered for numerous particles for each sample. These spectra, translated to composition, were then grouped according to element associations. These groupings were then compared to the results indicated by X-ray diffraction analysis. Samples a) and b) show varying analyses for different particles, illustrating the unique composition of specific crystalline material. In addition, chemical confirmation is made for the XRD identification. Samples c) and d) had a much more homogeneous particle composition with the significantly elevated TMs being common throughout the sample, but varying in amount. And sample e) was quite homogeneous chemically with respect to the elevated TMs; the average of the 54 particle analyses was very similar to that obtained for the bulk analysis with the exception of Ni; the elevated particle values may be due to interference from another element. Overall samples a) and b) can be considered to consist of specific crystaline phases to which solubility predictions can be made. Samples c) and d) may be able to be considered as specific crystalline phases with variable solid solution; and sample e) may consist of either amorphous phases or crystalline phases finer than the beam resolution of about 0.5 um.

SEQUENTIAL CHEMICAL EXTRACTIONS:

Table 4 gives results for sequential chemical extractions for the five samples and five steps. The data shown are percent TM extracted compared to the total TM extracted. Those steps resulting in significant TM mobilization are shown in **bold** values. In addition, the total TM mobilized, normalized to dry weight of sample, is shown for each TM studied.

It is most informative to compare the results of the extraction study to the XRD and EM results. The following summarizes similarities and differences:

Sample a: Large proportions of the TMs are tightly bound, being extractable only in steps 4 and 5. This is undoubtedly

Table 3. Results of elemental analysis on individual particles compared to compositional estimates made by X-ray diffraction analysis.

a) Smelter dust: 80 particles analyzed

Composition:	Percent analyzed:	XRD identified?:
Fe-Mg silicates	34	yes
Fe-oxides(magnetite,hematite)	21	yes
Pyrite	14	yes
Cu-Fe-sulfide	13	yes
Cu-Ni-Fe-sulfide	7	yes
Na-Al silicates	4	yes
Ni-Fe sulfide	3	yes
Ca-Al silicate	1	yes
K-Mg-Fe-Al silicate	1	no

b) Coal fly-ash: 90 particles analyzed

Composition:	Percent analyzed	XRD identified?:
Fe-Al silicate[1]	22	yes
Al-silicates(dickite,kaolinite)	14	yes
Fe-oxides(magnetite,hematite)	11	yes
Pyrophyllite	9	yes
pyrite	7	yes
anhydrite,gypsum	6	yes
nontronite	6	yes
quartz	3	yes
potassium feldspar	2	yes
forsterite	2	no
biotite	2	no
kyanite, sillimanite	2	yes
other	14	no

[1] - composition: SiO_2 46-70%; Al_2O_3 18-26%; Fe_2O_3 12-22%; possible minerals are sekaninaite, nontronite, ferro-gedrite, berthierine

Comment: Organic C is not accounted for; all TMs studied Cu, Ni, Zn, Cr, Pb, Cd, Hg) are less than 0.5%.

Table 3, continued

c) Steel flue dust: 80 particles analyzed

Composition:	Percent analyzed:	XRD identified?:
Zn-Fe oxide[1]	49	yes
Mn-Fe-Zn	13	in part
Fe oxides	6	yes
Mg-Fe silicate	6	no
Ca-Pb-Zn-Fe	5	no
Ca-Pb-Fe	5	no
Ca-Fe	3	no
Pb-Fe	1	yes
Pb-Zn-Fe	1	no
Zn-Fe-Si	1	no
Ca-Zn-Fe	1	no
Ca-Pb-Zn-Fe	1	no
Ca-Zn-Mn-Fe	1	no
Ca-Pb-Zn-Fe-Si	1	no

[1]- Zn/Fe ratios highly variable.

d) Iron foundry dust: 30 particles analyzed

Composition:	Percent analyzed:	XRD identified?:
Pb-Zn-Fe-Si	47	yes
Ca-Pb-Zn-Fe-Si	23	partly
Fe-Si (Pb,Zn)	10	no
Zn-Pb-Si	10	yes
Pb-Al-Fe-Si	3	no

Si, Fe, Mn, Pb and Zn are present in all particles analyzed and range between 11-29% SiO_2, 7-32% Fe_2O_3, 3-6% MnO, 2-21% Pb, and 4-11% Zn.

e) Plating sludge: 54 particles analyzed

Fe, Ca, S, Cu, Cr and Ni are ubiquitous to all particle analyses with ranges of 0.6-2% for Fe_2O_3, 3-9% for CaO, 7-15% for S, 3-27% for Cr, 3-8% for Ni and 5-14% for Cu. The average of the analyses for the 54 particles is very close to the bulk analysis suggesting that the sample is quite homogeneous:

	SiO_2	Fe_2O_3	CaO	S	Cr	Ni	Cu (%)
Part. average	5.8	1.3	5.0	12.6	11.1	9.1	8.7
Bulk analysis	4.0	1.3	6.3	10.1	10.4*	4.2*	8.1*

*- average

indicative of the TMs occuring as sulfide minerals. But there are also large fractions of Cu, Cd, Pb and Zn which are very poorly bound, being removed by desorption in step 1. The nature of the substrate is not known, but the iron oxides (hematite and magnetite) are likely candidates.

Sample b: Cu, Cd and Pb have significant proportions which are poorly bound, being desorbed quite readily. Whereas Cu is removed by exchange with Mg2+, major proportions of Ni, Cd, Pb, Zn, Mn and Cr are removed by a slightly acidic solution. Lesser amounts of Cu, Cd and Pb are strongly held, probably as sulfide minerals.

Sample c: Significant proportions of Cu, Cd, Pb and Zn can be mobilized by weakly acid solutions. This may reflect the dissolution of fine-grained metallic alloys and possibly oxides as identified by XRD. The majority of the TMs seem to be associated with strongly bound insoluble silicates and ferrites.

Sample d: Significant amounts of Cd and Mn can be easily removed by desorption with Mg^{2+}, whereas much of Cd, Pb and Zn can be removed by weak or stronger acid attack. The majority of Ni and all of Cu are more strongly bound, being removed only be strong oxidative or extreme acid attack. The weaker bound Cd, Pb and Zn are probably fractions sorbed on iron oxide surfaces, whereas the strongly held TMs reflect association with ferrites and silicates.

Sample e: All of the TMs are removed in the first three extraction steps, showing the extreme mobility of these elements. Steps 2 and 3, weak and stronger acid treatments, suggest that all of these TMs, would be mobile under slightly acidic conditions. This result agrees with the XRD data showing the TMs existing as acid soluble hydroxy-carbonate-sulfate salts.

COMMENTARY

The study of the bulk composition, crystalline characteristics, individual particle chemistry and extraction chemistry are used to characterize details of the solids from which conclusions regarding mobility of possibly toxic trace metals can be predicted. The initial study of five samples has shown that this approach is quite valuable in that details of the wastes are known, and each technique re-inforces (or negates) individual conclusions. For the most part, the sequential extraction results concur with the XRD and particle chemistry results. One very interesting difference found, however, was the large proportion of very poorly bound Cu, Pb and Zn in sample a; this sorbed fraction would not have been predicted by the other analyses. Since this is the most mobile fraction, additional study on the sorption-desorption of TMs (expecially Cu) needs to be carried out.

There are a number of additional developments in this analytical scheme that are required. First, an extraction step involving reduction is needed. This could be important for disposed wastes with sulfur and carbon; a step reflecting the redox potential for fermentation reactions would be appropriate. Second, the extraction scheme needs to be calibrated against known crystalline solids. In this study, greater confidence in the conclusions would have resulted if calibration of known sulfides, ferrites and TM-silicates were known. Third, as mentioned previously, matrix effects of TMs in elemental analysis of particles needs to be developed more thoroughly. There is evidence that Ni is over estimated, for example. More calibration systems need to be developed. Fourth, and perhaps most important, the mobilization of defined end-member substances need to be known better. There are very little data on the solubility or surface chemistry of trace metal ferrites and silicates, for example.

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TABLE 4. Results of sequential extraction on selected industrial waste samples. Results are given in percent of total extractable metal. Values in bold type reflect 15% or greater of total extractable metal. Step 1- exchangeable metal; step 2- "carbonate associated" (weak buffered acid); step 3- "Fe/Mn oxide" associated; step 4-"organic C" associated; step 5-residual.

	Cu	Ni	Cd	Pb	Zn	Mn	Cr
Sample A: Smelting dust:							
Step 1	**40**	5.7	**28**	**25**	**35**	12	4
Step 2	3.7	0.5	7.0	5.4	1.9	**61**	1
Step 3	0.4	1.2	1.3	2.7	3.1	2.7	**32**
Step 4	**45**	**49**	**21**	1.2	**20**	0.3	1
Step 5	11	**43**	**43**	**66**	**40**	**24**	**62**
Total extracted (mg/kg)	42000	24000	55	1490	2040	1800	416
Sample B: Coal Fly ash							
Step 1	**67**	3.9	**27**	**17**	5.2	0.5	1
Step 2	5.6	**81**	**30**	**35**	**27**	**89**	**82**
Step 3	9.0	4.1	3.0	14	10	0.5	1
Step 4	4.5	0.4	4.5	1.8	**46**	4.3	**15**
Step 5	**14**	11	**36**	**31**	12	5.4	2
Total extracted (mg/kg)	89	190	26	218	77	300	1680
Sample C: Steel flue dust							
Step 1	0.01	0.9	13	0.2	0.2	0.1	
Step 2	**15**	9.3	**42**	**47**	**39**	5.3	
Step 3	1.9	**15**	9.7	7.7	**18**	13	
Step 4	4.7	0.5	0.9	3.3	0.9	1.4	
Step 5	**79**	**74**	**35**	**42**	**41**	**80**	
Total extracted (mg/kg)	7090	1324	532	35000	153000	45000	
Sample D: Iron foundry dust							
Step 1	0.1	8.6	**28**	7.3	3.9	**15**	2
Step 2	0.1	**28**	**20**	**46**	**34**	8.1	**26**
Step 3	0.3	11	**32**	**34**	**34**	**26**	12
Step 4	**50**	2.4	5.3	4.2	1.7	6.1	1
Step 5	**49**	**50**	**15**	9.2	**26**	**45**	**58**
Total extracted (mg/kg)	8160	450	530	127000	57000	46000	940
Sample D: Plating sludge							
Step 1	0.1	0.6	**20**	10	1.6	2.1	
Step 2	**60**	**50**	**59**	**29**	**44**	**72**	
Step 3	**38**	**46**	**20**	**56**	**53**	**23**	
Step 4	2.0	3.6	1.4	1.3	0.5	1.4	
Step 5	0.02	0.02	0.6	3.6	1.5	2.1	
Total extracted (mg/kg)	87000	46000	32	16	204	200	

MODELLING THE MOVEMENT OF VAPOURS FROM HAZARDOUS LIQUIDS IN SOIL

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Key words: Hazardous Spills, Soil Contamination, Vapours.

ABSTRACT

The discharge of hazardous liquids to soil, either intentionally or by accident, has been the subject of much concern in recent years. Attention has focussed upon tracking the liquid on the surface and through the soil, assessing the impact of the incident on the environment and creating a remedial response.

Since many hazardous liquids are volatile to some degree, concern must exist for the movement of hazardous vapours through soil from the spill or discharge zone. Very little quantitative information has been published about the problem, although reports of volatile contaminants have been reported at some sites. Consequently, work was undertaken to develop a theoretical model to provide a means of exploring the nature of hazardous vapour movement in soil.

The model is based on the Darcy and constitutive equations for intergranular porous media flow. The equations have been solved analytically for simple site situations and numerically with both finite difference and finite element methods for more complex spill and site geometries. Accommodation has been made for realistic venting of the soil surface, variability in soil composition and moisture content, multiple source configurations such as "pancakes" on the zone of saturation and flexibility in the type of liquid under study.

The search for field or experimental data to calibrate and verify the model has not been successful. However, the model has been used to study vapour movement under many possible spill situations through simulation. The impact on vapour transport in soil of liquid type, liquid source configuration, soil condition and ground surface configuration has been studied and reported upon.

MODELLING THE MOVEMENT OF VAPOURS FROM HAZARDOUS LIQUIDS IN SOIL

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This paper describes the progress of a research project carried out at the University of Waterloo under the combined sponsorship of the Ontario Ministry of the Environment (MOE) and NSERC. The work is in the second year of a three year programme to study the behavior of immiscible liquids spilled onto soil. It has been partitioned into three phases, a literature review, the development of mathematical models to simulate liquid behavior and a series of experiments to explore and quantify various aspects of this behavior. A paper describing the accomplishments of the first few months of the project was presented previously (Farquhar and McBean, 1984) and this is a follow-up of that presentation.

1. Literature Review

The literature review phase of this project will be active until the completion of the work. However, an extensive review of literature available at the time was conducted at the outset of the project to provide an information base line. This has now been printed in draft report form and has been submitted for review to the MOE Liaison Committee of this Project. It should be available for use in the early part of 1986.

An Information Storage/Retrieval System (IS/RS) was created for this work using the IBM DBASE II package. It has been used for information management in the context of the literature review. The system allows information about papers and reports to be stored on disks in the form of key words, a descriptive paragraph, authors and title.

Retrieval of information comes through reference to key words and authors. A detailed user's manual for the IS/RS has been prepared and is available for use by others.

2. Simulation Model Development

Three sets of simulation models have been produced either in whole or in part in the context of this project:

Spill Simulation Model (Wall, 1984).

Two Phase Porous Media Flow Model (Osborne and Sykes, 1985).

Vapour Transport in Soil Model (Allan, 1985).

All models have, as their core, computerized numerical solutions to the partial differential equations which describe the various fluid transport systems. All models have been completed to the point where computer codes have been prepared and verified with analytical solutions. All models have experienced only limited testing because of an almost complete lack of laboratory or field data against which to make comparisons. As a consequence of this, experimentation will be carried out during this project to provide data for comparison with simulation model results. A portion of this work is described subsequently.

Simulation models are an essential part of this project because, once properly tested and calibrated, they can be of great value:

1. to examine immiscible liquid behavior over a wide range of soil and liquid properties, field and environmental conditions, spill configurations, etc. for which individual equivalent experimentation would be extremely expensive,
2. to test the sensitivity of liquid behavior to ranges of specific input parameter values,

3. to extend documented trends at existing spill sites, and
4. to assist in the management of spills by evaluating responses to various proposed remedial measures.

The Spill Simulation Model is currently in active use in support of experiments to study liquid spills under both laboratory and field situations to be discussed subsequently. It is also being revised to improve the infiltration component and to include the effect which interfacial tension between the liquid and the surface has on the spread of the liquid. Both the Spill Simulation and the Porous Media Flow Models have been described in previous papers (Farquhar and McBean, 1984; Osborne and Sykes, 1985). The Vapour Transport in Soil Model has just recently been completed and is therefore described in more detail below.

2.1 Vapour Transport in Soil Model

Surface spills and underground leaks of volatile immiscible liquids represent potentially serious health hazards not the least of which is due to the release and spread of toxic and/or flammable vapours. Research on this topic has been undertaken in order to study the volatilization and subsequent vapour migration from spilled or buried immiscible liquids and to create a comprehensive mathematical model to describe these processes. Because of the complexity of the processes involved and the heterogeneous properties of the subsurface, the model uses a numerical solution of the governing equations.

Three-dimensional (3-D) numerical modelling of contaminant transport is an extremely complex and expensive process. However, in many field situations, it is often possible to assume uniformity in one of the three dimensions and thus to use a much less complex 2-D model. A 2-D model was developed in this work.

2.1.1 Mathematical Development

Vapour flux is most easily dealt with on a molar basis. The molar flux (J) equals the number of moles transported across a unit area in unit time $(\frac{\text{moles}}{m^2\ s})$. Hydraulic gradients result in advective flux while concentration gradients result in diffusive flux. Mechanical mixing is produced by irregular flow paths and varying pore size distribution in a porous medium. Mechanical mixing and diffusion make up dispersive flux. The molar flux of a gas mixture is then a sum of the advective and dispersive fluxes.

For two-dimensional flow, flux can be expressed as:

$$J_i = cq_i - D_{ij} \frac{\partial c}{\partial x_j} \qquad \begin{array}{l} i = 1,2 \\ j = 1,2 \end{array} \qquad (1)$$

where;

c = molar concentration

D_{ij} = dispersion tensor (m^2/s)

The Darcy velocity (q) is defined as the total flow through a porous medium over the cross sectional area of the medium perpendicular to the direction of flow. The two-dimensional form of the Darcy equation is given as:

$$q_i = \frac{k_{ij}}{\mu} \quad \frac{\partial(egz+p)}{\partial x_j} \qquad (2)$$

The eg term represents the gravitational component of the flux. Many researchers have neglected the body force in gas flow [Scheidegger, 1974]. The model described in this work allows the user either to include or to ignore the body force term.

The Darcy equation does not hold for turbulent flow (ie. with Reynold's numbers greater than 5 to 10 [Freeze and Cherry, 1979]). Mohsen [1978] showed that gas flow under a pressure head of 3 kPa has a Reynold's number of less than one. Pressure heads greater than this are not common in the subsurface. Thus it can be concluded that the Darcy equation is generally applicable.

If more than one non-mixing fluid is present in the pore spaces, a relative permeability constant must be used. This constant reflects the fact that when a pore contains one fluid, its permeability to another immiscible fluid is reduced relative to the single fluid case. For the case of vapour flow in soil, water and gas share the available pore space. The actual permeability of a medium to a fluid in two-phase flow is the relative permeability (k_g) times the saturation or intrinsic permeability (k_{g_i}). Bear [1972] found that;

where the s_g term is the degree of gaseous saturation in the pore spaces and B is an exponent to be determined experimentally.

The dispersion tensor (D_{ij}) used in this work was developed using formulae developed by Bear [1972, 1979].

$$D_{xx} = a_L \frac{q_x^2}{|q|} + a_T \frac{q_z^2}{|q|} + D_{e_x} \qquad (4)$$

$$D_{zz} = a_T \frac{q_x^2}{|q|} + a_L \frac{q_z^2}{|q|} + D_{e_z} \qquad (5)$$

$$D_{xz} = D_{xz} = (a_L - a_T) \frac{q_x q_z}{|q|} \qquad (6)$$

where L = longitudinal or x direction

T = transverse or z direction

For a porous medium like soil, an effective or apparent diffusion coefficient (D_e) is used. The effective diffusion coefficient takes into account the effect of the porous medium on the rate of diffusion.

The effective diffusion coefficient is a function of the open-to-air diffusion coefficient (D') and soil properties. The model allows the use of the following equation from Greenland and Hayes [1981].

$$D_e = \varepsilon^{\alpha} \cdot D' \tag{7}$$

where α is an experimental coefficient

This equation would not be required if experimentally determined diffusion coefficients were available.

It is impractical to model porous media fluid transport on a microscopic scale because to do so, the arrangement and geometry of each pore space would have to be determined. For the model described herein, a continuum approach is applicable. By continuity, the mass balance of a control volume of a porous medium experiencing vapour transport is:

$$\varepsilon \frac{\partial c}{\partial t} = \frac{\partial}{\partial x_i} \left(D_{ij} \frac{\partial c}{\partial x_j}\right) - q_i \frac{\partial c}{\partial x_i} \tag{8}$$

This equation has no source, sink or reaction terms. Thus the vapour is considered to be conservative.

2.1.2 Solution of Equations

Numerical solutions are used to approximate the exact solutions of partial differential equations (PDE's) with given boundary and initial conditions. They are used because the PDE's are too complex for most field situations to be solved by analytical means.

The two numerical solution techniques most frequently used today are the finite difference and the finite element methods. The finite difference technique is the simpler method but it is less flexible. The finite element technique is more suited for complicated geometries, anisotropies, and complicated boundary conditions of most field soil conditions and was thus selected for this work.

The soil domain in which vapour migration occurs is a rectagular section of soil with constant thickness (Figure 1). The four sides of the domain must have known boundary conditions in order to obtain a numerical solution. The Dirichlet boundary condition allows concentrations to be specified at the boundary. The Neumann boundary condition accounts for the case in which vapour flux is specified at the boundary. A special type of boundary condition involves specifying a mass transfer coefficient to control vapour movement from the soil domain to the atmosphere. The vapour flux is then the mass transfer coefficient times the concentration gradient at the boundary. This transfer is controlled by a stagnant or laminar layer of air at the soil surface. Tinsley [1979] stated that the rate of diffusion from the surface "depends on the diffusion coefficient in air and the width of this layer of stagnant air".

A rough approximation of the mass transfer of the vapours from the soil to the atmosphere is given by Thibodeaux [1981] as:

$$J_{atm} = H\ (c - c_{atm}) \tag{9}$$

with

H = Empirical mass transfer coefficient $(\frac{m}{s})$ [Thibodeaux, 1981]

This relationship is a linear simplification of the diffusion of the vapour through the laminar layer. It is an acceptable simplification if the depth of the layer is much smaller than the depth of the domain.

The finite element method of numerical solution requires that a continuous domain is discretized into subdomains or elements. These elements are bounded by nodes. In the solution for a domain, nodal values of the dependent variable (eg. concentration) are determined. The elemental values are related to the nodal values by interpolation functions. The interpolation functions approximate the behaviour of the dependent variable within the element. Because of the relative simplicity of the PDE solved in this work, linear triangular elements and linear interpolation functions were chosen for its numerical solution. The Galerkin of weighted residuals was used to solve the PDE.

2.1.3 Model Testing

To ensure that a computer coded model solves the given partial differential equations properly, its results should be compared to analytical solutions for simplified forms of the equations. Two analytical solutions were used in this work to test the model, the first, a simple one-dimensional system and the second, a more complex, two-dimensional system.

An analytical solution for the one-dimensional advection dispersion equation in a semi-infinite homogeneous medium (ie. x= 0->∞) with a Dirichlet point source boundary was used. This solution, commonly called the Ogata-Banks solution [Freeze and Cherry, 1979], is given as;

$$\varepsilon \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - q \frac{\partial c}{\partial x} \tag{10}$$

This is analogous to flow along a highly permeable stratum.

The model results are shown in comparison with the analytical solution in Figure 2. The agreement is excellent.

Cleary [1978] developed an analytical solution for the two-dimensional advection dispersion equation. The soil medium is homogeneous, semi-infinite in x, and infinite in z. The source is a Dirichlet strip source along the y axis. The governing equation is as follows:

$$\varepsilon \frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2} + D_z \frac{\partial^2 c}{\partial z^2} - q_x \frac{\partial c}{\partial x} - q_z \frac{\partial c}{\partial z} \tag{11}$$

Good comparisons between various runs and the Cleary solution can be seen in Figure 3. These favourable comparisons verified the accuracy of the model.

2.1.4 Comparisons With Field Data

The model was used to simulate actual field cases of vapour migration in soil. Since no data were available on vapours arising from hazardous liquids, comparisons were made with the migration of methane gas (CH) from a landfill. Field data from the Mississauga landfill were used in this case [Metcalfe, 1982].

The hydrogeologic conditions of the site are shown in Figure 1. Because the simulation started in September and continued into the winter, the first half of the simulation had a radiation-type boundary, open at the ground surface, while the second half had an impermeable ground surface due to a frozen cover.

The results of the model simulation are shown in the concentration contours of Figures 4 and 5. The effect of the changing ground surface boundary can be seen in the contours. During the "open months", the atmosphere acts as a sink and slows gas transport. The concentrations at the ground surface are very small. In the "closed months", gas movement is more pronounced because the closed boundary allows gas to build up at the surface and then forces it to move outward from the landfill. The simulated contours closely approximated the actual field measurements [Metcalfe, 1982], as seen in Figure 5. The results show that the model can be used to help predict gas movement in the field.

2.1.5 Typical Simulations

Since no field data dealing with vapours from spilled liquids could be found, simulations of typical cases were undertaken. The liquid used was benzene because of its widespread use in industry and the availability of data on fluid properties [Environment Canada 1984].

Benzene is lighter than, and immiscible in water. Therefore, when a volume of benzene liquid reaches a water table, it tends to spread out or to 'pancake' on the water table. As it rests on the water table it releases vapours which will migrate through the surrounding soil. It was this vapour movement that was simulated.

The domain used in the simulation is shown in Figure 6. Hydrogeologic properties for the domain were chosen using common soil types [Freeze and Cherry 1979].

The Dirichlet source is shown in shown in Figure 7. It was assumed that the benzene solution was at saturation with a saturation vapour pressure of .1 atmospheres and a mole fraction of .10 obtained for the Dirichlet nodes. A slight pressure gradient of 0.4 Pa/m was imposed on the soil section.

The simulation was run for a period of 300 hours. The concentration contours for 100, 200 and 300 hours are shown in Figure 7. Again, the open ground surface boundary prevented any significant concentration buildup near the top of the domain. Because of the high permeability of the lower layer, the benzene plume moves most rapidly in this layer. As well, a small pressure gradient in the x direction can greatly affect the rate of movement of a vapour in soil.

The second benzene simulation was done assuming a source held in soil. Besides the different sources, the main difference between this simulation and the previous one is that there are no pressure gradients. This was done to observe the advection due solely to diffusion and body forces.

The Dirichlet concentrations were set at 5%, to reflect a 50% saturated solution. The Dirichlet nodes and the benzene concentration contours for 100, 200, and 300 hours are shown in Figure 8. The contours show the slow rate of lateral movement of the benzene vapours. This is because only diffusion and body forces provide advective flux. The vapour quickly reaches the watertable but then its outward movement becomes very sluggish. These simulations and the favourable comparison with the CH migration data from the Mississauga Landfill demonstrate the value of the Vapour Transport in Soil Model.

3. Experimentation

Very little information is available to describe the behavior of immiscible liquids spilled onto soil in terms of spreading on the surface, infiltration and movement through both saturated and unsaturated soil. Some work has been done with petroleum products of various types [Schwille, 1984] but this is limited in both extent and accessiblity. Consequently, it was proposed that experiments be performed in this project to provide some of the missing data. It was intended that the data collected also be used to test and calibrate the models created in this study.

3.1 Artificial Spills

The first set of experiments have dealt with the spilling of liquids onto a flat, impervious surface. The radii of the spill and the hydraulic jump as well as the fluid depths were measured with respect to time through the use of video recordings. Experiments performed to date have made use of a declining rate spill involving liquid volumes up to 5 l and liquid types including water, kerosene and mineral oil. The spill occurred through an orifice with a diameter = 1.0 cm and from a height of 20.0 cm.

The data from one experiment in which 5 l of kerosene were spilled are shown in Figure 9 in terms of spill and hydraulic jump radius with respect to time (the former increased while the latter decreased). The simulation of this spill through the use of the Spill Simulation Model described above is also shown. Excellent agreement between the actual and simulated hydraulic jump locations is evident. However, the model predicted a greater spill radius than was actually measured. The reason for this appears to be related to the interfacial attraction between the fluid and the surface upon which the fluid is spilled. The model accounts for most of the important physical properties of the problem - height of spill, declining flow rate, momentum in the fluid, mass conservation, surface roughness, etc. It does not however account for interfacial forces between the fluid and the surface. It was found that, under identical conditions, a spill of kerosene created a larger radius than a spill of water. It was observed that the contact angle between the liquid and the painted flat surface was greater for water than for kerosene and was therefore able to support a greater depth of ponded fluid and thus a smaller radius. Revisions to the Spill Simulation Model to accommodate this condition are now being studied.

A second set of liquid spill experiments to be carried out in the field have been initiated in co-operation with a private engineering corporation. Specific volumes of various immiscible liquids will be spilled onto vegetated soils under controlled loading conditions. Measurements will be taken to determine spill size, rates of infiltration and movement through the soil and liquid retention within the pores. The results of this work will be reported upon subsequently.

3.2 Thermal Conductivity Probe

Experiments have continued for the development of a thermal conductivity probe which could be used in the non-destructive detection of fluids in soil. The need for such a probe was identified during the design of experiments to study the movement of immiscible liquids and water through soil. It is necessary in this work to detect the displacement of one liquid by another within the soil structure and to do so without stopping and/or taking the system apart for analysis. Because different liquids conduct heat at different rates, the concept of the conductivity probe was considered.

A schematic diagram of the probes used in this study are shown in Figure 10. Although several designs have been worked on, they all consist of a variable D.C. current source and a temperature senser/recorder outside the soil with a heating coil surrounding a termister (or a thermometer) within the soil. Direct current is pulsed through the coil and the maximum temperature is recorded through the termister/senser/recorder system. Higher maximum temperatures occur when the soil contains fluids with a low thermal conductivity (such as air) and vice versa with fluids having a high thermal conductivity (such as water). This is shown in Figure 11 which presents experimental results in which a probe was immersed in air, water and mineral oil in various mixtures. The thermal conductivity (TC) of air < mineral oil < water. The results expressed as maximum temperature achieved (DT in 'C) are plotted as bar charts with DT varying inversely with TC as expected. The results also show that DT's vary when the probe is immersed in water to various percentages of immersion with the overlying fluid being air or mineral oil. The experiments were performed in sequence as shown from left to right in Figure 11. The results show that the technique has the potential to detect the partial extent of one fluid displacing another in soil.

Figure 12 shows the results of experiments in which a plastic column (length = 30 cm, diameter = 9.5 cm) containing unsaturated Ottawa sand and a probe located within the sand at an elevation extending from 12.6 cm to 14.3 cm from the bottom of the sand. Initially, the DT values averaged about 10.5°C with the soil pores containing mostly air. Subsequently water was allowed to pass upward through the soil so that the zone of saturation moved upward eventually to be in contact with the probe. The capillary fringe above the zone of saturation averaged approximately 1.5 cm in height. The data show that, as the capillary fringe reached the probe, the DT's began to decrease due to the greater TC of the water. When the soil surrounding the probe became saturated with water, the T's reduced to values near 1.8° C. These data suggest that the probe may be useful in determining relative fluid saturation in soil.

Work on the probe is continuing in order to experiment with various designs and operating conditions and to standardize probe responses to various conditions.

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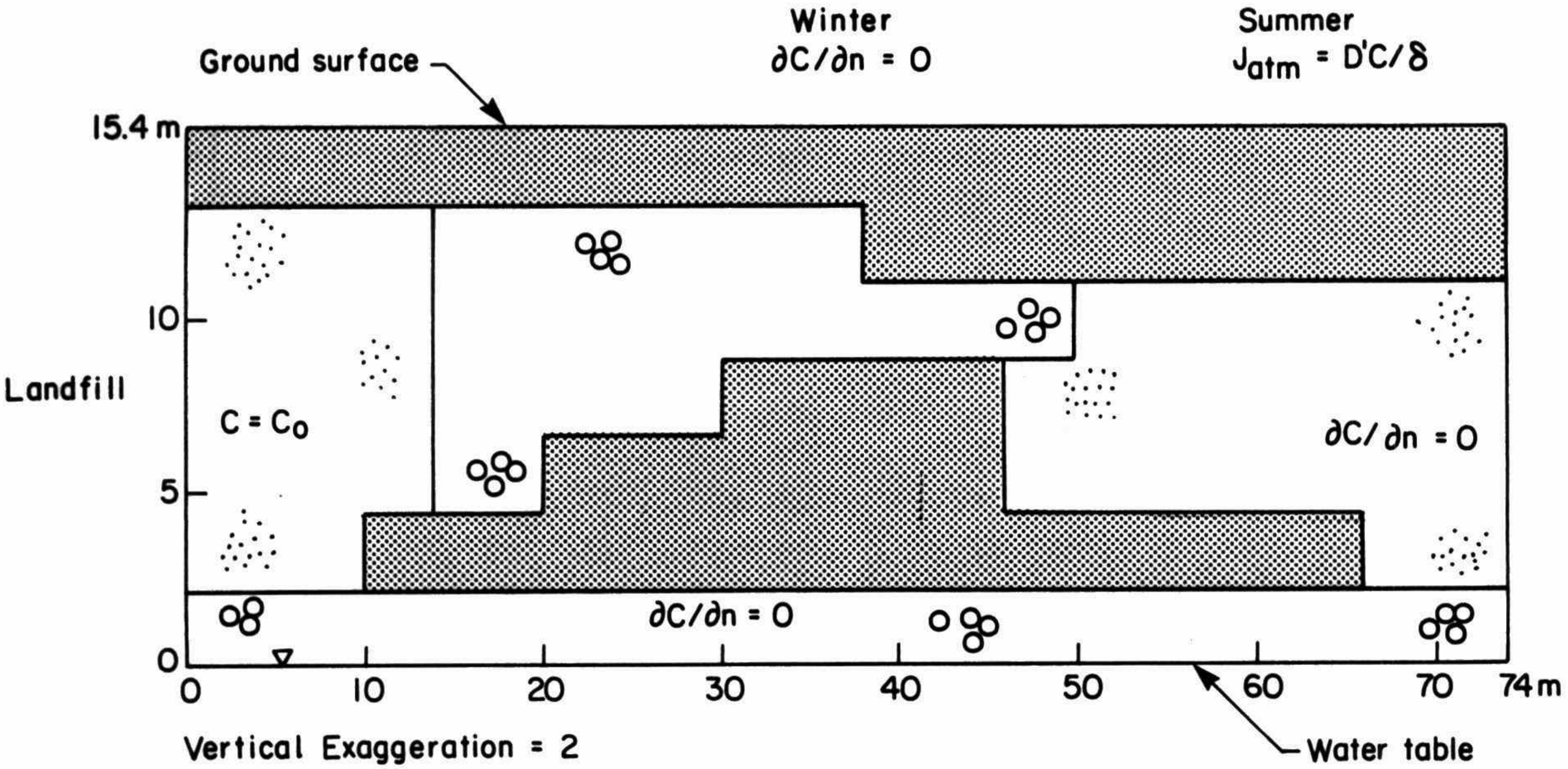
Figure 1 Typical Soil Domain For Modelling Vapour Transport


Winter
$\partial C/\partial n = 0$
Summer
$J_{atm} = D'C/\delta$
Ground surface
15.4 m
10
5
0
Landfill
$C = C_o$
$\partial C/\partial n = 0$
$\partial C/\partial n = 0$
0
10
20
30
40
50
60
70
74 m
Vertical Exaggeration = 2
Water table

Soil Type		Permeability (m^2)	Porosity	Field Capacity
Gravel/Coarse Sand	○○	1×10^{-10}	.3	.05
Medium Sand	░	5×10^{-12}	.35	.05
Fine Sand/Silt	▒	1×10^{-13}	.45	.25

FIGURE 2
RUNS 1 AND 7 VS OGATA BANKS (500 HRS)

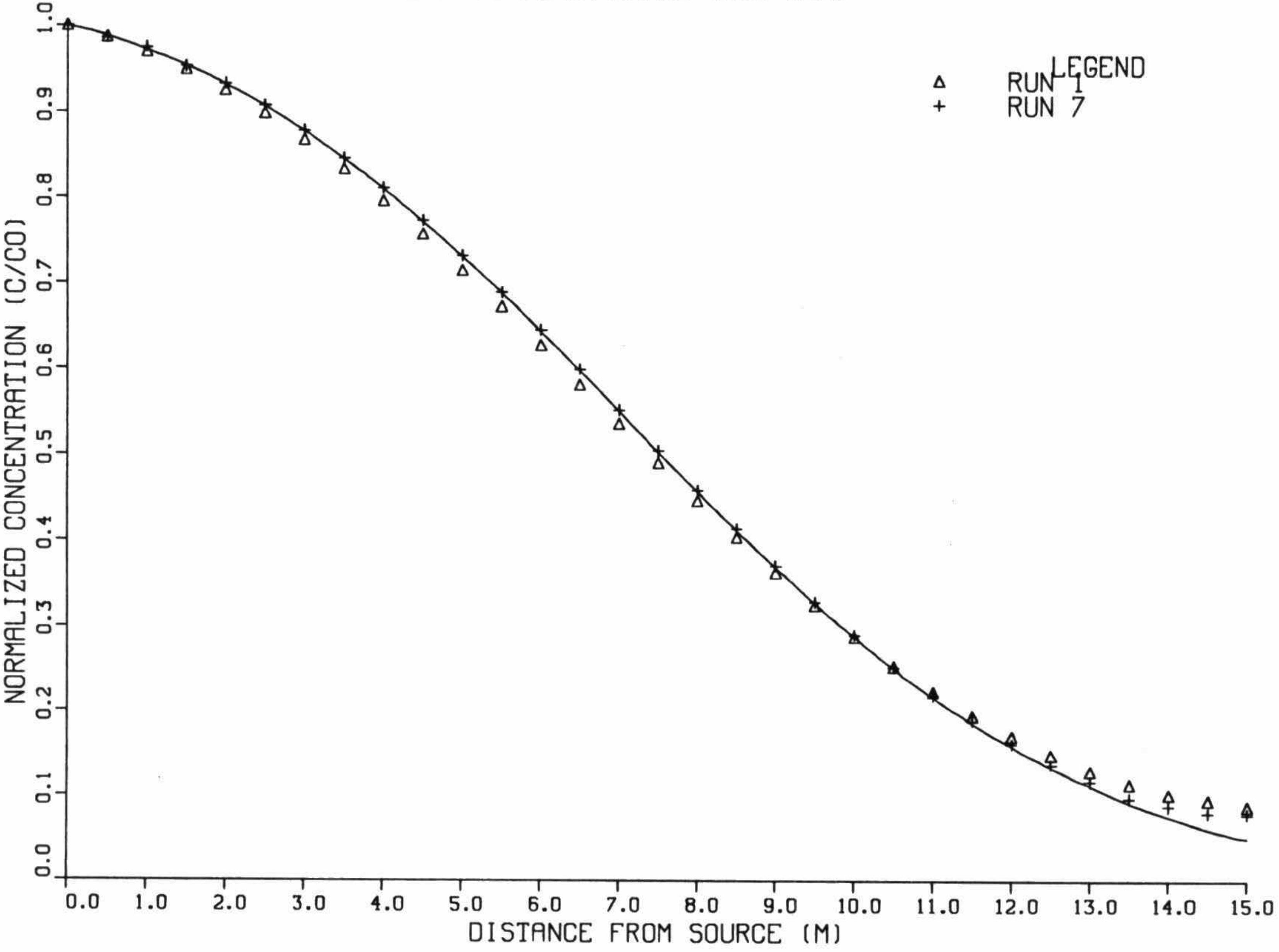


FIGURE 3

RUNS 1 AND 2 VS CLEARY (300 HOURS)

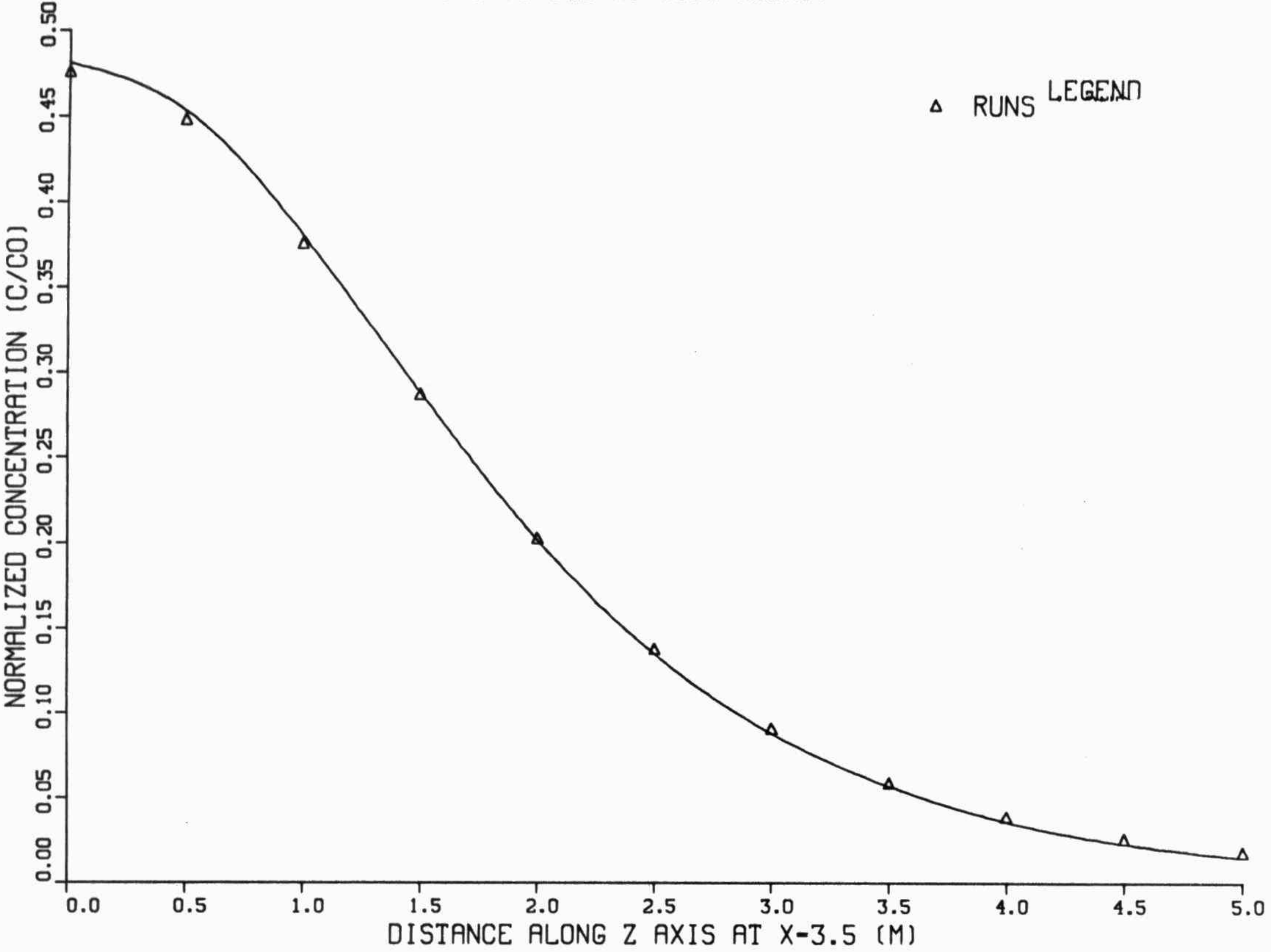


Figure 4 Simulated Methane Concentrations (% by Volume) in Soil Migrating from the Mississauga Landfill; Open to the Atmosphere

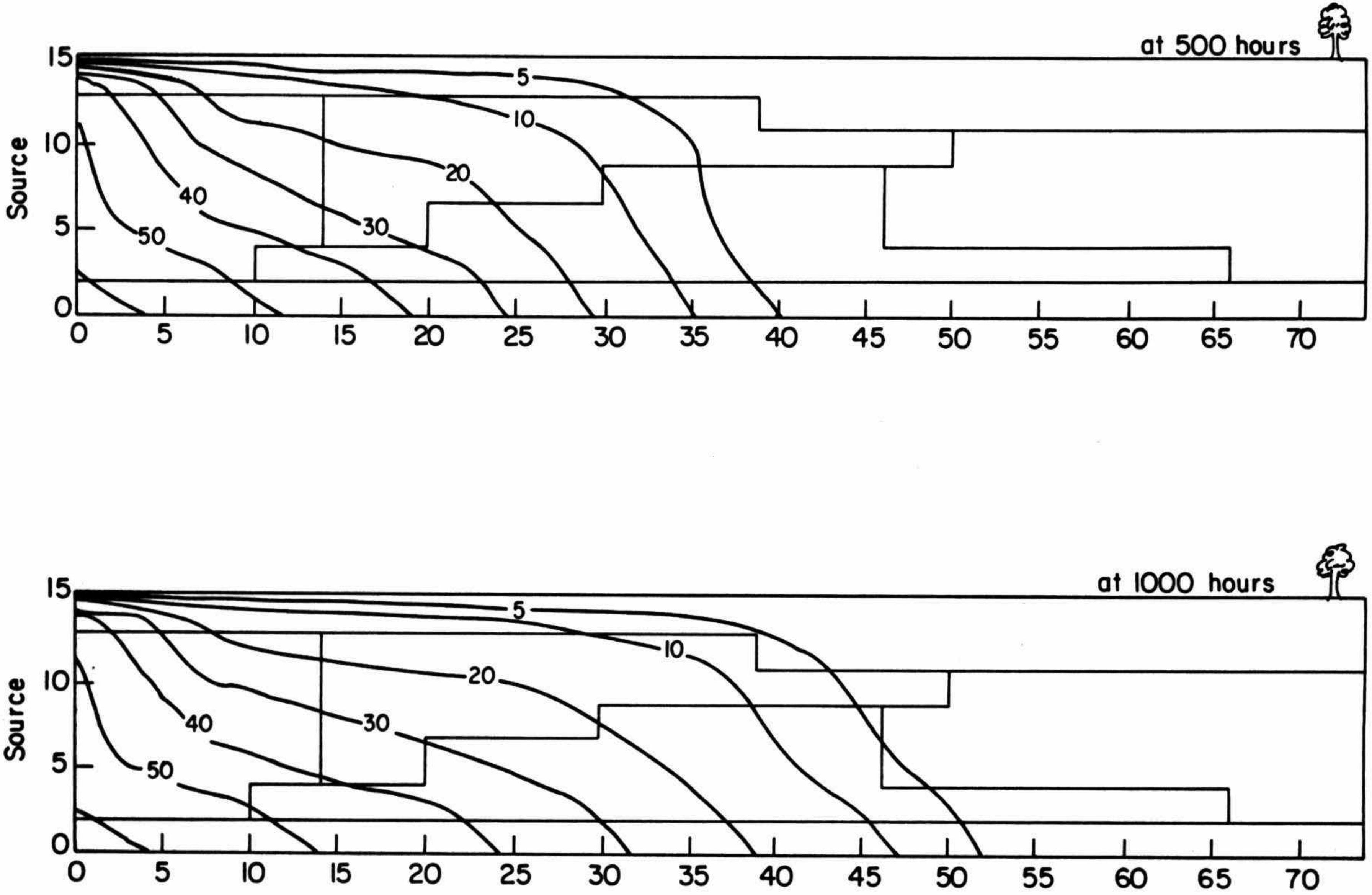


Figure 5 Simulated Methane Concentrations (% by Volume) in Soil Migrating from the Mississauga Landfill; Closed to the Atmosphere

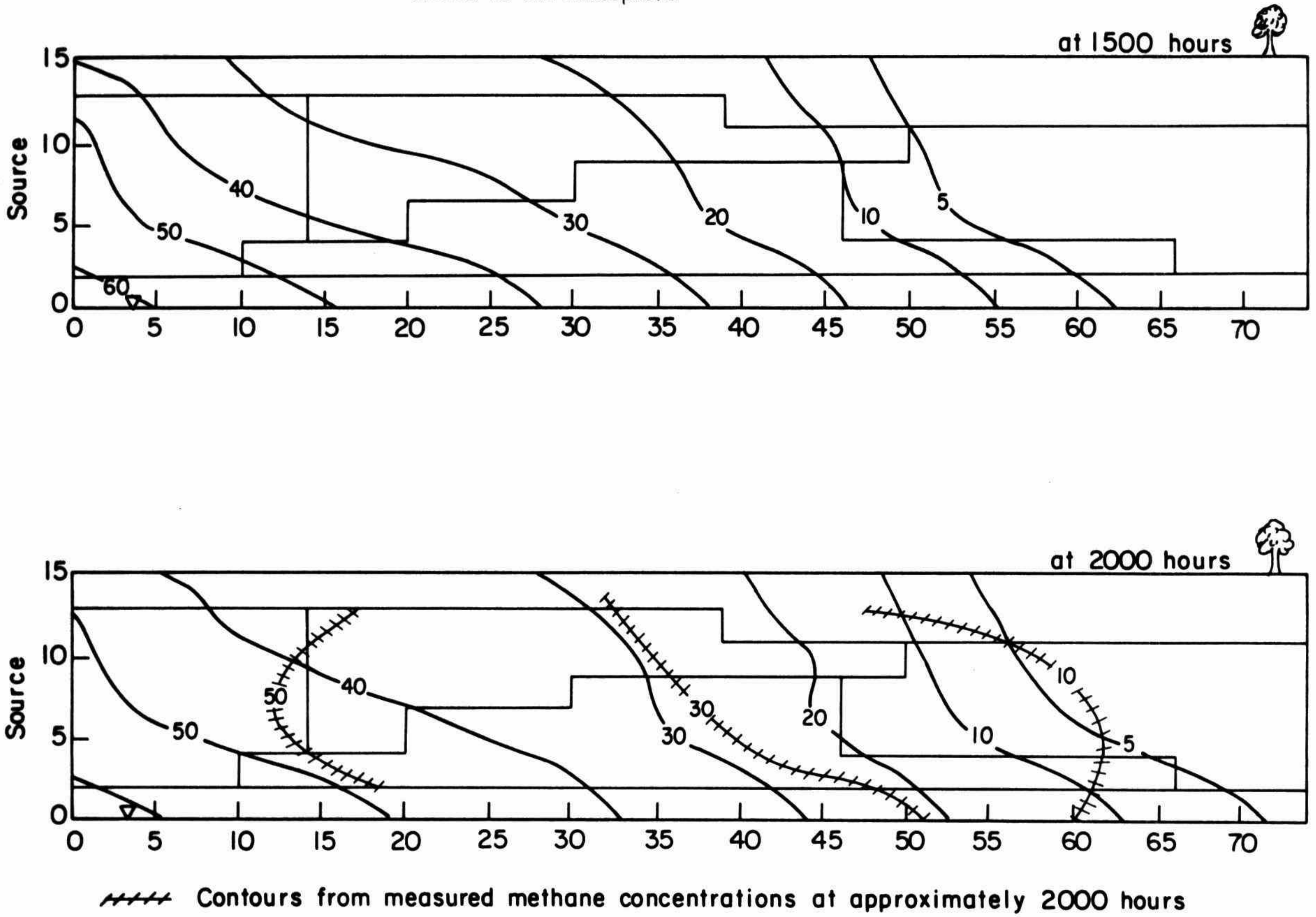
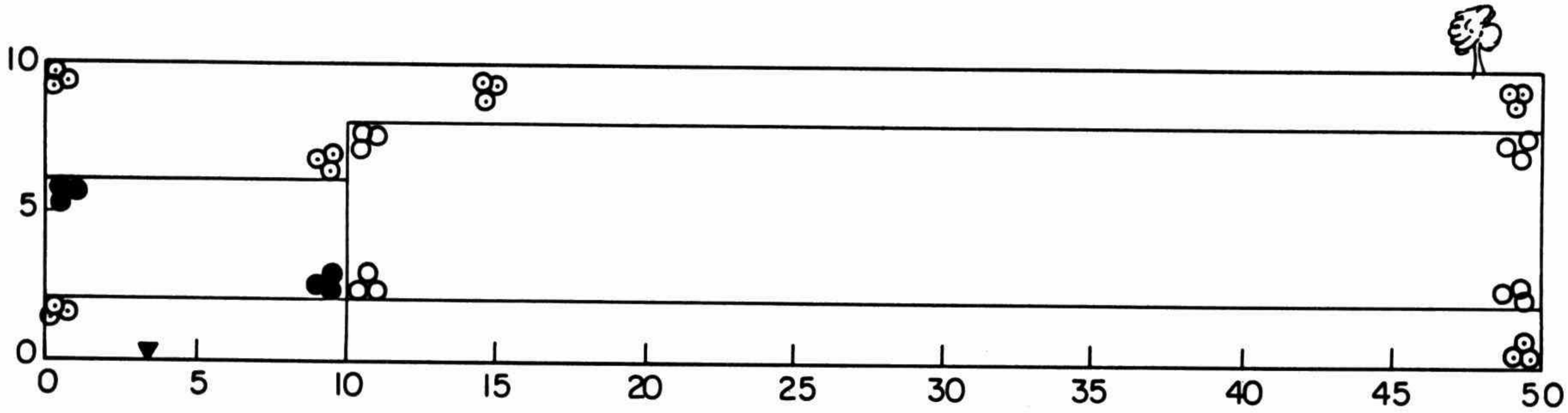


Figure 6 Soil Domain Used for the Simulation of Benzene Vapours in the Soil



Soil Type	Permeability (m^2)	Air-Filled Porosity
● Gravel/clean sand	10^{-10}	.30
⊙ Gravel/coarse sand	10^{-9}	.35
○ Clean sand	10^{-11}	.30

Figure 7 Simulation of Benzene Vapour Migration from a Pancake Source Resting on the Ground Water Table

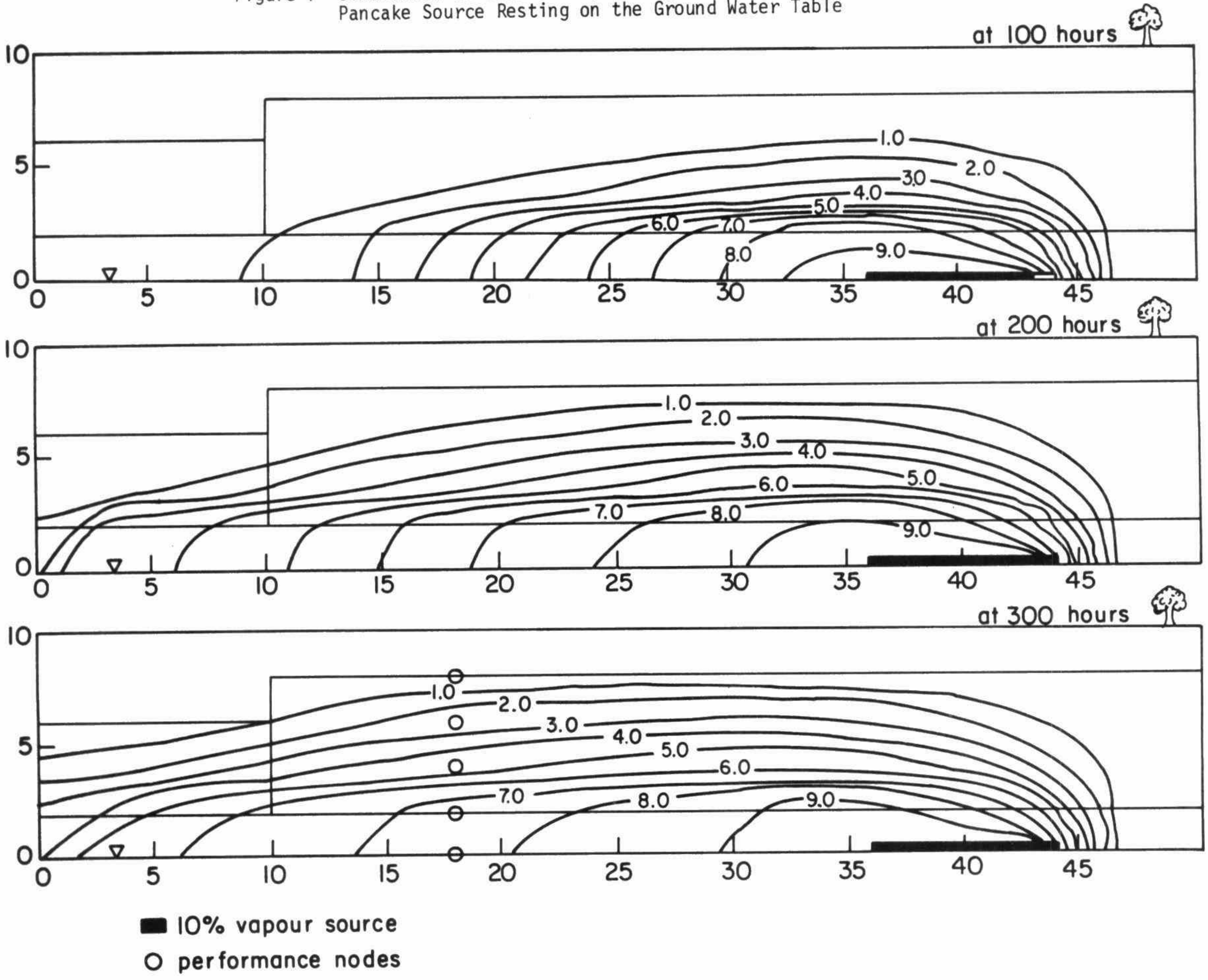


Figure 8 Simulation of Benzene Vapour Migration from a Source in Unsaturated Soil

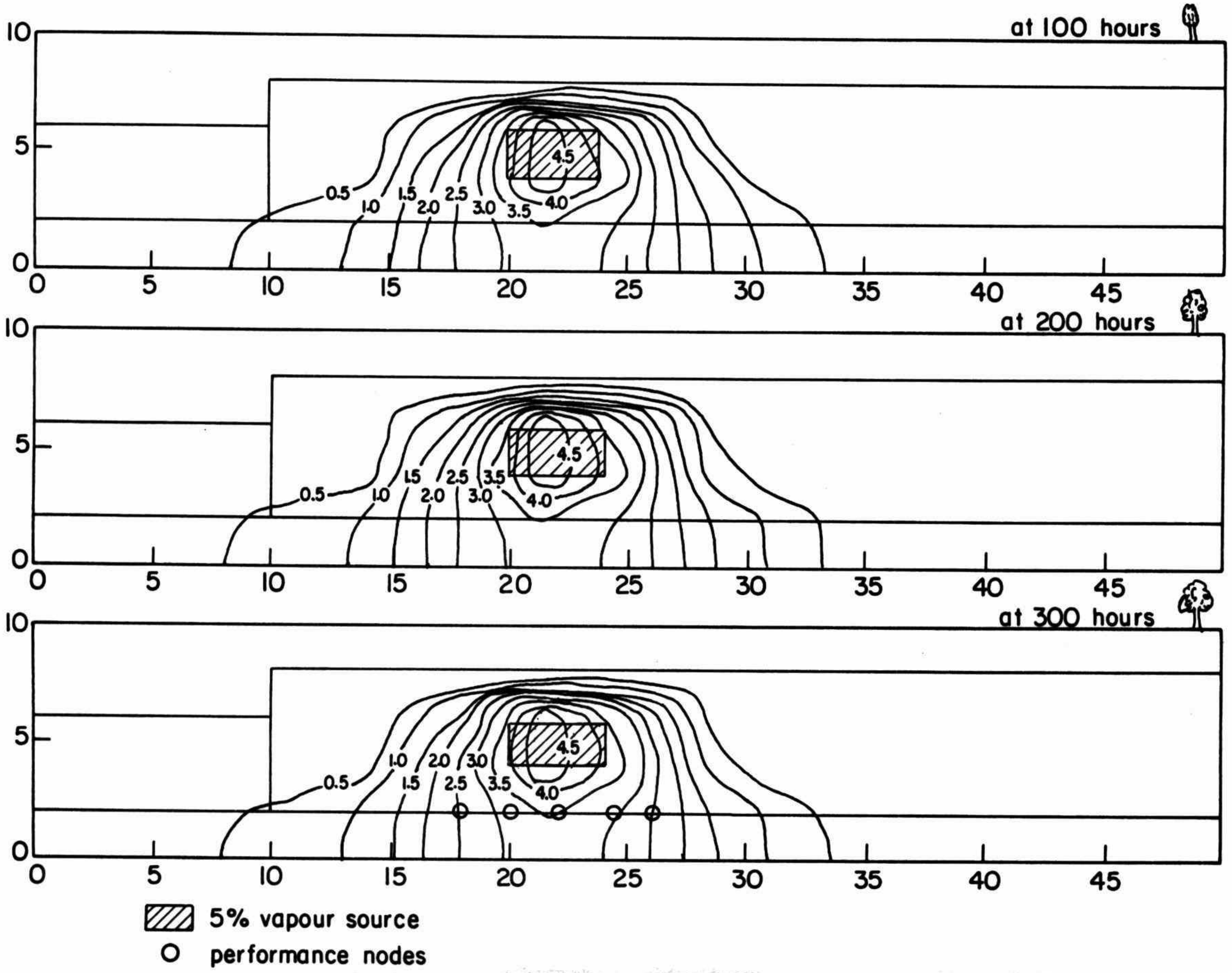


Figure 9 Plots of Predicted vs Measured Hydraulic Jump and Spill Front

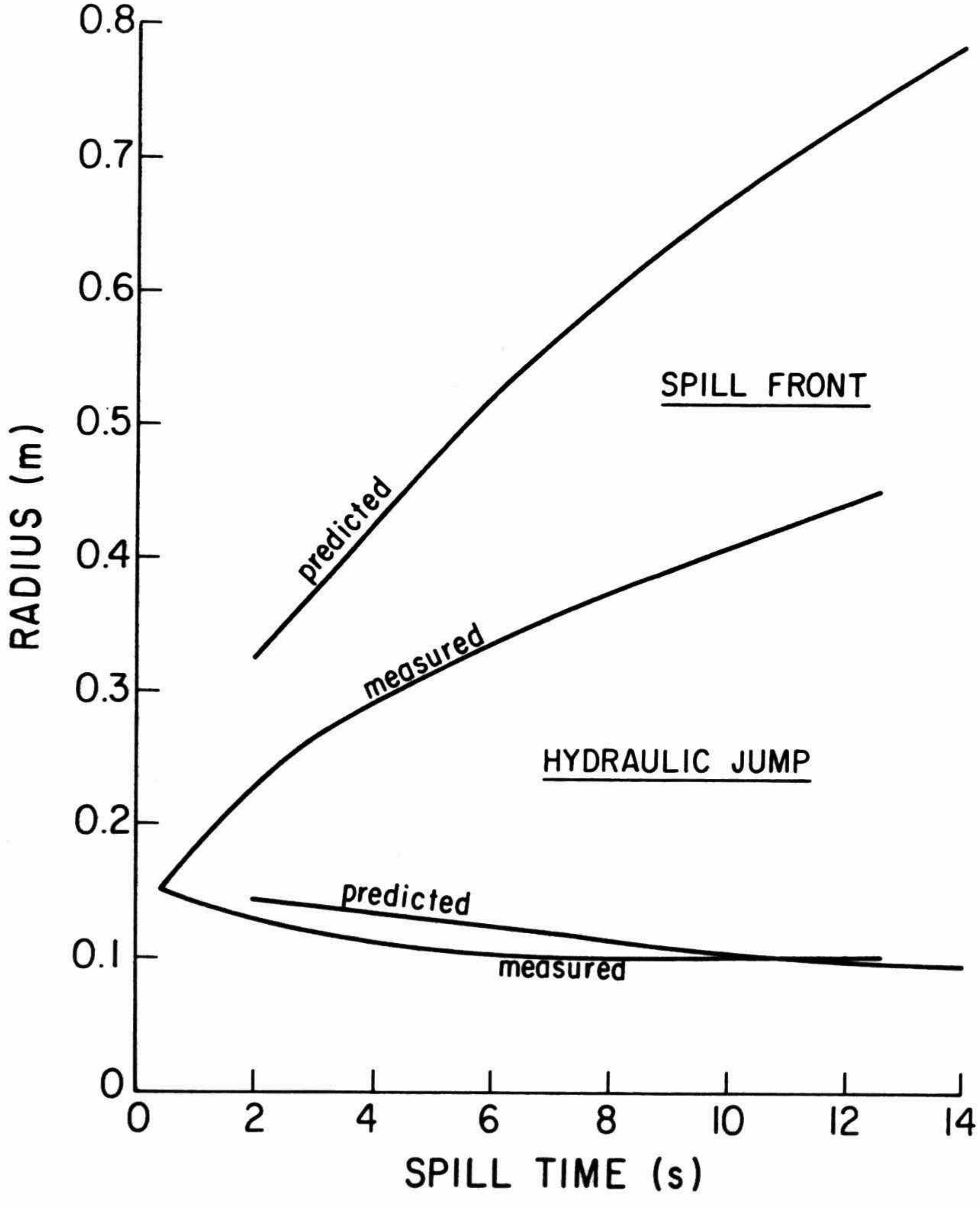


Figure 10 Schematic Diagram of Thermal Conductivity Probe

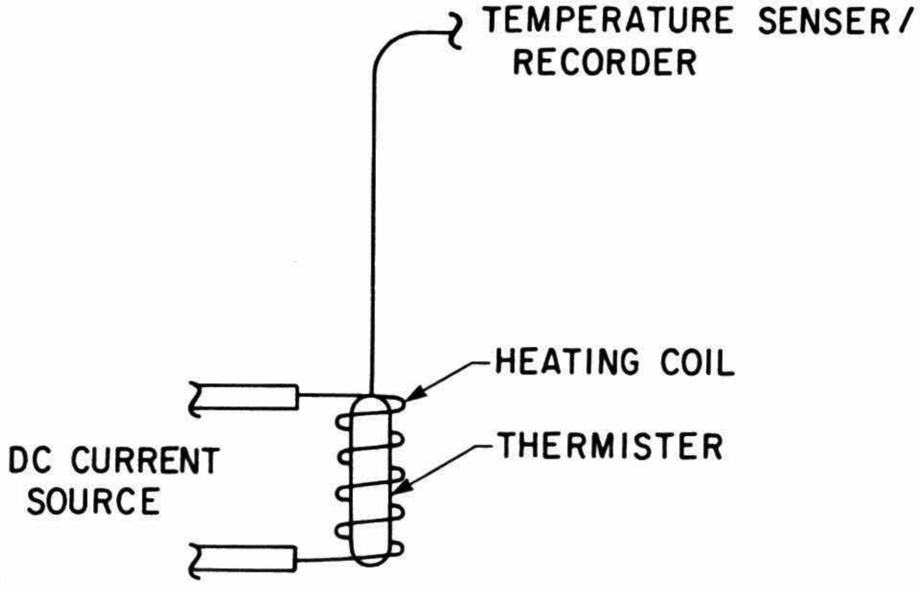


Figure 11 Response of Thermal Conductivity Probe to Various Fluid Mixture

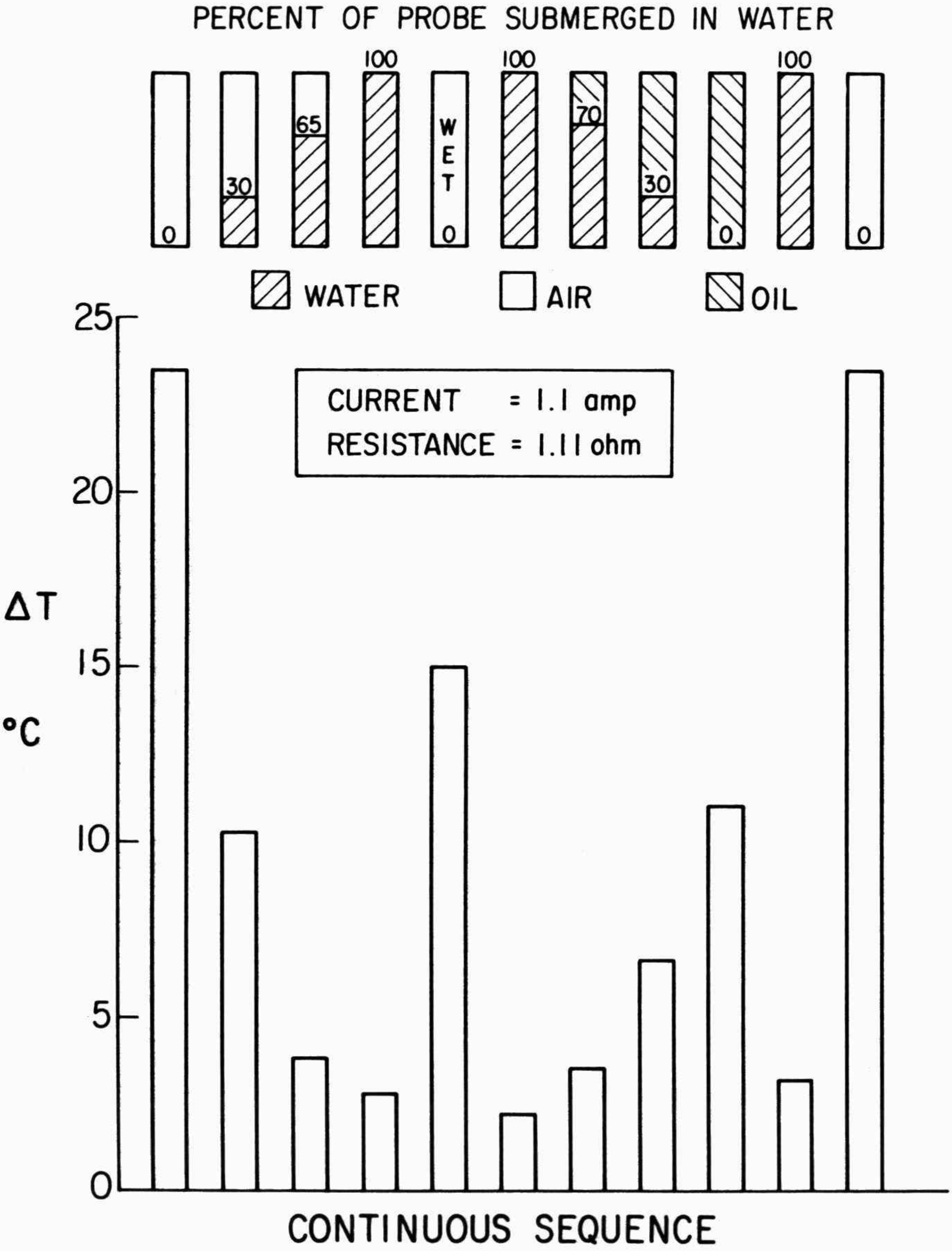
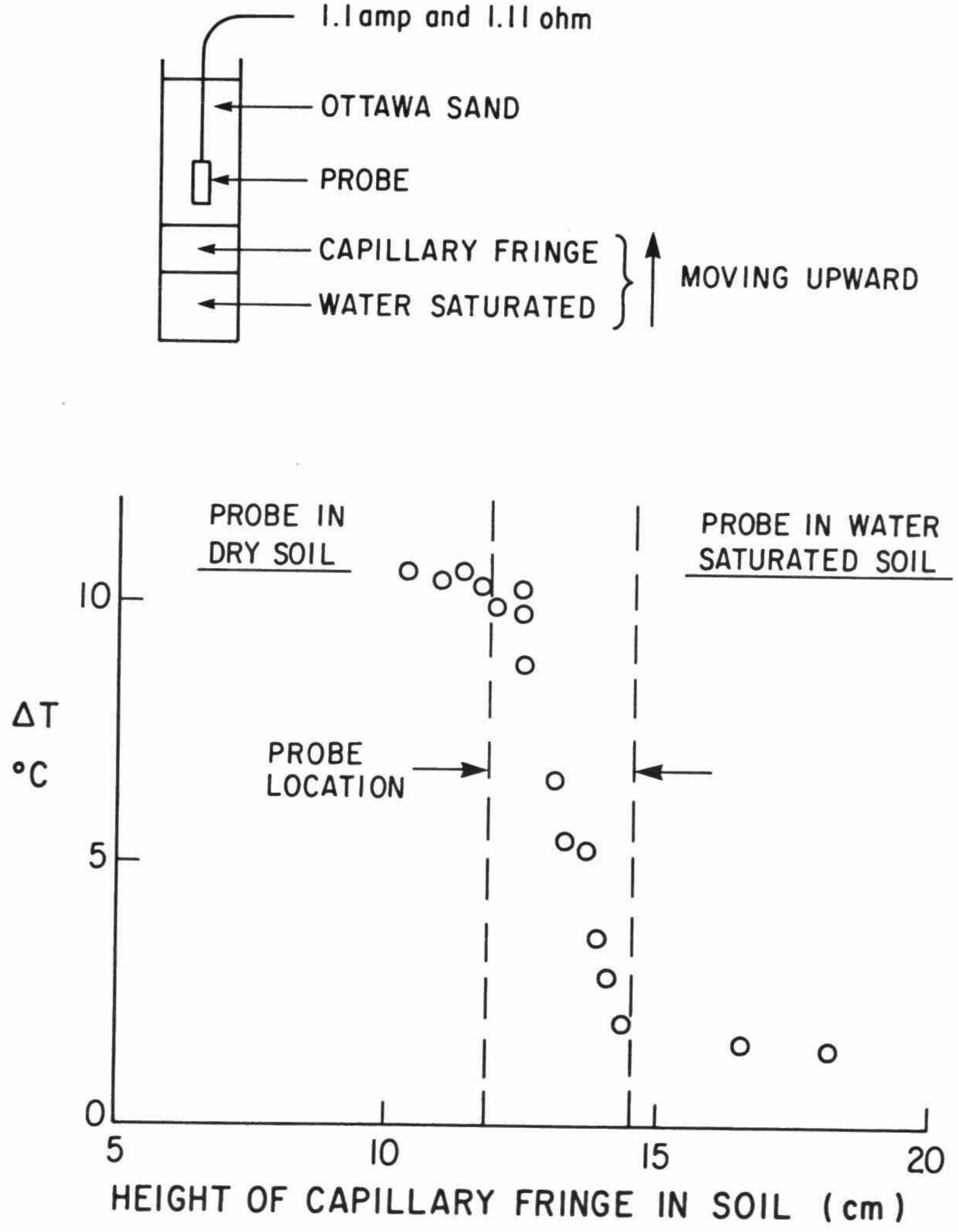


Figure 12 Response of Thermal Conductivity Probe to the Passage of Variable Water Content in Soil



POSSIBLE EFFECTS ON GROUNDWATER QUALITY OF THE USE OF LIQUID INDUSTRIAL WASTES FOR DUST CONTROL ON ONTARIO ROADS

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Key words: Groundwater, Liquid Industrial Wastes, Dust Control, Road Oiling, PCB.

ABSTRACT

This study involved a review of the literature and other information concerning dust control practices in Ontario, with a view to evaluating the potential environmental consequences of those practices. Major sources and distributors of dust suppressants were identified and trends in the use of the various materials were indicated. Presently, there are no reported instances of groundwater contamination as a result of dust control practices, though two cases of surface water contamination by PCBs have been attributed to the use of waste oil. An evaluation of the potential for groundwater contamination is presently limited by a lack of detailed chemical data for most of the suppressants used. It is clear, however, that waste oil has the greatest potential for contamination, while salt brine, in some instances, could lead to local contamination of groundwater by inorganic constituents. Though there is no indication that dust control represents a serious threat to groundwater quality, in order to further resolve the questions, site specific investigations would be required.

INTRODUCTION

Over the past decade, major efforts have been directed at the identification of chemicals and practices that can have detrimental effects on the environment. These efforts will undoubtedly continue as we are faced with an ever-expanding list of potential contaminants. It is therefore appropriate that the potential effect on the environment of the chemicals and practices used for dust control on unpaved roads be investigated.

In 1983, over 136 million liters of liquids, having diverse compositions, were applied to unpaved roads in Ontario. This has been an ongoing practice for many years, and in addition to providing dust control, has served as a convenient and cost-effective method for disposing of a variety of industrial waste products. In spite of the obvious benefits, isolated instances have been reported where the use of dust suppressants has led to degradation of local environments. Suns et al. (1980) reported the presence of polychlorinated biphenyls (PCB) in fish residues of 12 Muskoka area lakes. It was found that 71% of the samples from lakes that received runoff from oiled roads contained PCB concentrations in excess of the wild-life guidelines, whereas concentrations in areas where roads were not oiled were much lower. It has also been reported (Theilheimer, 1983) that bottom sediments of Lake Clear in Sepastopol township contain high PCB concentrations in the vicinity of an unpaved road. In these examples, there is no indication that the existing regulations concerning the application of dust suppressants were not followed.

The most notable and most highly publicized instance of dust suppressants leading to serious impairment of the environment concerns the town of Times Beach in Missouri (Wilson, 1984). In the early 1970's, a distributor of dust suppressant reportedly sprayed the streets of Times Beach with used lubricating oil mixed with industrial sludge containing dioxin (2,3,7,8-tetrachlorodibenzo-p-dioxin). Subsequent testing by the U.S. Environmental Protection Agency in December 1982 confirmed the presence of dioxin in Times Beach soils, and later in December of the same year, flooding caused the basements of many homes to become contaminated with dioxin. The town was subsequently evacuated and designated as a priority toxic cleanup site. Investigations and cleanup at the site are continuing.

The Times Beach situation can not be viewed as typical or wide spread in that the practice that led to the problem was not approved, and indeed, is not an approved practice in Ontario. The incident does however serve as a dramatic demonstration of the serious consequences that can result when sufficient care in screening the product is not taken, or when regulatory controls are not followed.

The major purpose of this study was to evaluate the potential for dust suppression practices in Ontario to contribute to groundwater contamination. In that very few site specific studies have been conducted, the approach taken was to identify and quantify the materials used for dust control, and to determine the chemical composition of these materials. The potential for groundwater contamination was evaluated on the basis of concentrations of specific constituents and their mobility in geologic materials.

The study was based entirely on information available in the literature and on discussions with personnel in the Ministries of the Environment and Transportation and Communication and with representatives of the industry. Though various trends in the use of dust suppressants were identified, and potential sources of environmental concern, there was insufficient information available to draw firm conclusions. As a consequence, the most significant result on the study may have been to provide direction and priorities for further research. The complete study is described in the report by Gillham et al. (1985). A summary of that report is included here.

DUST SUPPRESSANT USE IN ONTARIO

In 1983 approximately 30,000 km of unpaved roads in Ontario were treated with dust suppressants. Calcium chloride, used oil and salt brine are the major suppressants used, while sulphite liquors from pulp and paper mills occupy a very small proportion of the market. Commercial products such as Bond-All, Petrotac, Tembind and Coherex, though tested in some instances, are presently not used commercially and will therefore not be considered further in this report.

Calcium Chloride

Calcium chloride is the most widely used dust suppressant. It is a hygroscopic, deliquescent salt, and for use in dust control, is obtained as a byproduct of soda-ash production. It is distributed either as solid flakes or as a liquid. The flakes consist of relatively pure di-hydrated crystals, containing 77% calcium chloride, while liquids used for dust control generally contain about 35% calcium chloride and 65% water.

Allied Chemical in Amherstburg, Ontario is the only source of calcium chloride used for dust suppression in Ontario. There are four major distributors of calcium chloride across the province, all receiving their supply from Allied Chemical.

As indicated in Table 1 and 2 and in Figure 1, calcium chloride is the most widely distributed of the dust suppressants, and in 1983, accounted for about 89% of the total length of road treated by dust suppressants. Because calcium chloride is produced in the form of flakes, shipment and storage are relatively convenient and inexpensive. The ease of shipment, combined with its effectiveness as a dust suppressant and its consistent quality make calcium chloride highly competative with the other major dust suppressants. As a result, there has been a continuing growth in its use over the past several years. Based only on the amounts used, it is apparent that calcium chloride must be given top priority in considering the environmental consequences of the use of dust suppressants.

Used Oil

Used oil is the second most commonly used material for dust control. Sources of used oil are highly diverse, but in general, include crankcase drainage from automotive, railway, marine and farm equipment, and oil used in industry for cutting, machining and insulation purposes.

The number of distributors of used oil has declined in recent years, with only seven being identified in 1984. By far the largest distributor, accounting for about 80% of the total used oil-dust control market is Canam Oil Services of Breslau, Ontario.

As shown in Tables 1 and 2, in 1983 used oil accounted for about 12% of the total volume of dust suppressants used in Ontario and about 6.6% of the total length of road treated. The distribution of use is indicated in Table 1 and in Figure 2. Though the use of oil is quite widely distributed, as suggested by Figure 2, the most concentrated use appears to be in the north-central portion of southern Ontario, and in particular, in the Muskoka area.

The use of oil for dust control has declined substantially over the past ten years. This decline is reflected to some extent in a comparison of the distribution of use in 1983 (Figure 2) with the distribution of use in 1978 (Figure 3). Though strictly comparable figures were not obtained, it is estimated that the decline in use between 1978 and 1983 was on the order of 50%. Several factors have contributed to this trend including greater economic incentives for recycling oil, and greater competition from the other dust suppressant materials.

Salt Brines

Salt brines are produced from oil and natural-gas wells in south- western Ontario, and are being used increasingly as dust suppressants. They have a variable composition, containing salts primarily of calcium, sodium, potassium and magnesium. Calcium chloride, the only salt having dust suppressant capabilities is generally present at concentrations ranging from 5 to 15%. In addition to the major salt constitutents, brines may contain natural organic chemicals and heavy metals in trace amounts, depending upon the geology of the formations from which they are derived.

Referring to Tables 1 and 2, brines represent about 15% of the total volume of dust suppressant used on Ontario roads in 1983, and accounted for about 4.2% of the total length of roads treated. As shown in Figure 4, the distribution of use is limited to areas close to the source, principally south-western Ontario. Brines occur as liquids having relatively low concentrations of calcium chloride (5-15%). Thus, although the initial cost is low, transportation and storage costs are high. This undoubtedly accounts for the limited distribution.

Sulphite Liquor

Sulphite liquor, also referred to as black liquor, S.S.L., or lignosulphonate, is a waste product of the pulp and paper industry. The major constituents of the waste solutions are biodegradable lignin-related compounds;

however the chemistry varies depending upon the process used by a particular mill.

Though there is a very large potential source of sulphite liquor (estimated to be about 3.4 x 10^9 liters per year) as shown in Tables 1 and 2, this material accounts for only 1% of the total volume of dust suppressant used, representing about 0.003% of the total length of road treated. The only use of sulphite liquor identified was in the Trenton area (Figure 5).

CHEMICAL CHARACTERISTICS AND POTENTIAL FOR GROUNDWATER CONTAMINATION

Calcium Chloride

Table 3 lists the inorganic constituents that have been identified in the various dust suppressant materials. As indicated, the only constituents that have been identified for calcium chloride are calcium and chloride. Though the method of production results in a relatively pure product, it is inconceivable that there would not be trace amounts of other elements present. Though it is quite unlikely that these would be present at environmentally significant concentrations, a trace analysis of the calcium chloride material should be undertaken. It is not expected that the calcium chloride would contain organic contaminants, and indeed none have been reported.

Calcium is the major cation present in most groundwaters and is generally present at concentrations that are in equilibrium with solid phases such as carbonate minerals. As a result, calcium added to the soil zone through the use of calcium chloride for dust control should not have a significant effect on the calcium concentration of groundwaters. As a highly soluble monovalent anion, chloride is mobile in the soil and groundwater zones, and indeed, it is reasonable to expect local increases in chloride concentration in the vicinity of roads treated with calcium chloride. Based on Table 3, chloride in calcium chloride solutions and for dust control would exceed the recommended drinking water standard (250 mg/l) by a factor of about 1000. However, from a consideration of the quantities applied, annual precipitation and allowing for water losses by evapotranspiration, it was estimated that the concentration of chloride reaching the groundwater zone would be at least 100 times less than the applied concentration. Although this dilution factor has not been documented, it is believed to be reasonable for the purpose of this report, and to be quite conservative. Allowing for the one hundred-fold dilution, the concentration of chloride reaching the groundwater zone could still exceed the drinking water standard by a factor of 10. Considering the local nature of the source and that further dilution would occur within the groundwater zone, it appears unlikely that chloride would represent a serious threat to groundwater quality. Though of questionable logic, in view of the quantities used, it could further be argued that the chloride from calcium chloride used for dust control would be of much less environmental significance than chloride from the use of sodium chloride as a highway deicer.

Salt Brine

As shown in Table 3, the composition of salt brine is highly variable, being dependent upon the geologic formation from which it is withdrawn. It is also quite likely that the variability would be even greater were the results of more analyses available, and that the list of constituents would be much longer if more complete analyses were available.

Of the elements listed in Table 3, after allowing for a 100 x dilution, four exceed drinking water standards, iron, manganese, sodium and chloride.

Iron and manganese both occur in geologic materials as cationic species and as oxyhydroxides. Both are relatively immobile under oxidizing conditions, and tend to be more mobile under reducing conditions. Both of these elements occur naturally at significant concentrations in most natural geologic materials, and that added through the application of salt brine would cause an imperceptible change in concentration. The iron and manganese contained in salt brine should therefore not represent a risk to local groundwater environments.

After 100 x dilution, sodium in salt bring could exceed drinking water standards (20 mg/l) by a factor as great as 5.000x. As a monovalent cation of high solubility, ion exchange is the principal geochemical process leading to reduced mobility of sodium. Nevertheless, in view of the potentially high concentrations in the brine solutions, it is reasonable to expect that in some hydrogeologic environments, particularly those with sandy soil materials and shallow water tables, the application of brine for dust control could lead to sodium contamination of the local environment.

As in the case of calcium chloride, salt brine could also lead to chloride contamination. In that the chloride concentrations are somewhat higher, the severity of contamination could be greater than that associated with calcium chloride. No analyses for organic constituents of salt brine have been reported.

Used Oil

Used oil contains a wide range of both inorganic and organic constituents. As shown in Table 3, the concentrations of inorganic constituents are highly variable. From Table 3, and using a 100 x dilution factor, eight constituents of used oil could result in groundwater concentrations in excess of drinking water standards. These include

barium
cadmium
chromium
lead
copper
iron
manganese
zinc

Of these, cadmium, chromium, lead, copper and zinc are listed as EPA Priority

Pollutants and therefore deserve particular consideration.

In that the concentration range for most elements is exceedingly broad, it is difficult to ascertain the relative importance of the various elements. Based only on concentration, the data suggest that of the inorganics, lead may be of greatest environmental concern. Including the dilution factor, the maximum lead concentration reported in used automotive oil (2.0 mg/l) exceed the drinking-water limit (0.05 mg/l) by a factor of about 4000. In most other cases, the maximum reported values after dilution exceed the drinking water limit by factors ranging from about 5 to 25.

Cadmium and lead both have a single oxidation state of +2 and under normal groundwater conditions would occur as the divalent ions, as carbonate precipitates under oxidizing conditions or sulphide precipitates under reducing conditions. Because the mineral phases have very low solubilities, concentrations in the solution phase are generally very low. As a result, the cadmium and lead of used oil could contribute to the contamination of surface soils, but it is quite unlikely that they would have a significant effect on groundwater quality.

Copper and zinc also have oxidtion states of +2 under normal groundwater conditions, and generally occur in the solution phase as divalent cations, or in the solid phase as precipitated hydroxides. Because of both ion exchange and precipitation processes, these elements tend to be immobile in soil materials and thus their occurrence in used oil is not likely to have a negative effect on groundwater quality.

Under oxidizing conditions, chromium tends to occur in the +6 oxidation state while under reducing conditions +3 state tends to dominate. Under reducing conditions, a highly insoluble oxide (Cr_2O_3) is formed and thus the chromium tends to be immobile. However, under oxidizing, mobile anionic species such as $HCrO_4^-$ or CrO^{2-}_4 tend to predominate. It is therefore reasonable to expect that some portion of the chromium in used oil could reach the groundwater zone. Nevertheless, in view of the relatively low concentrations of chromium in waste oil, and the relatively small volume of the source, it is difficult to envision a situation where the chromium in waste oil used as a dust suppressant would result in a significant deterioration in groundwater quality.

As discussed for salt brine, it is quite unlikely that the iron and manganese of waste oil would lead to groundwater contamination.

The organic chemistry of waste oils potentially available for use as dust suppressant is extremely complex. This results from not only the natural complexity of the oil fraction of crude oil and its refined products but also the wide range of addatives or contaminants added through its commercial and industrial use.

A complete listing of the organic constituents of waste oil is not included here (see Gillham et al. 1985); however, Table 4 shows the general composition of waste oil according to classes based on general structural similarities.

Factors that will determine the potential for a particular constituent to result in groundwater contamination include solubility, volatilization, sorption, chemical transformation and biodegradation. Though it is not practical, or even possible, to evaluate all the constituents in terms of these factors, an initial screening can be made on the basis of solubility. Table 5 was calculated on the basis of concentrations of specific parameters reported to be in waste oil, and the aqueous solubilities of these parameters, and ranks the constituents in order of decresing concentration that is likely to occur in the aqueous phase. Numerous assumptions were made in preparing the table and thus its quantitative validity and in some cases the ranking is quite uncertain. Nevertheless it suggests that the monocromatic hydrocarbons, halogenated hydrocarbons and alkanes are likely to be in highest concentration in infiltrating water that has been in contact with road oil. It also suggests that several compounds of current environmental concern such as PCB's and most PAH's are likely to be present at very low concentrations in the aqueous phase.

Many organic constituents can be lost from the oil or the aqueous phase to the gas phase by volatilization. Many of the constituents of Table 5 have vapor pressures that could lead to significant volatilization, with the halogenated hydrocarbons, benzene and hexane being among the most volatile. As a result, some re-ranking of Table 5 could be required to derive a better estimate of concentrations in percolating water.

Sorption processes result in a transfer of organic solutes from the solution phase to the solid phase and thus tends to reduce their aqueous mobility. The potential for sorption tends to increase as the aqueous solubility decreases, and thus the sorption process would tend to reinforce the ranking of Table 5 with respect to concentrations in infiltrating water.

Organic compounds which readily biodegrade present little groundwater pollution potential. Unfortunately, biodegradation rates have a complex dependency on environmental factors and so are difficult to predict.

Based on the available information, and acknowledging a high degree of uncertainty, it is suggested that almost all non-halogenated hydrocarbons found in waste oil have some potential to biodegrade aerobically with PAH's and PCB's tending to have the least potential for biodegradation. Most halogenated hydrocarbons have some potential for anaerobic degradation but little potential under aerobic conditions.

Recognizing that solubility, sorption chemical transformations and biodegradation are interactive process and are strongly dependant upon the local environment, it is exceedingly difficult to evaluate the potential for organic contamination of groundwater by constituents of oil used for dust control. In that used oil contains several constituents that have drinking water limits in the parts per billion range, it appears that site-specific studies of this topic would be warranted.

Sulphite Liquor

Table 3 shows sulphite liquor to contain relatively few inorganic constituents, and none at concentrations that would be of environmental concern. However, in studies of a groundwater contaminant plume associated with a sulphite liquor lagoon, Robertson et al. (1984) found chloride, sodium and potassium to be at substantially elevated concentrations. This suggests the data of Table 3 to be incomplete, or that the samples analysed are not representative of all sources of sulphite liquor. The inorganic constituents identified by Robertson et al. are not generally viewed as serious groundwater contaminants, and in view of the limited extent of the source, there is little possibility for the material, when used for dust control, to contribute significantly to groundwater contamination. Nevertheless, more thorough inorganic characterization of sulphite liquors used for dust control is warranted.

The organics reported in sulphite liquor are dominantly breakdown-products of lignin including simple carbohydrates (sugars) and acidic products including fatty acids. Detailed analysis for trace organics is not available but would be required to fully evaluate the groundwater pollution potential of sulphite liquor.

The highly soluble sugars have little potential for sorptive retardation, but are readily metabolized in aerobic environments. Though the sugars are not toxic, their biodegradation could lead to anaerobic conditions in the groundwater zone which could affect the mobility of other toxic ions.

Lignin degradation products include phenol, which is quite mobile and a recognized pollutant of concern. Many of the other products are readily biodegraded which would minimize their groundwater pollution potential except, perhaps, for producing high BOD. Fatty acids are rather insoluble and are likely greatly retarded by sorption processes. They are less biodegradable, in general, than sugars but should not pose serious groundwater quality problems.

Of the specific organic compounds associated with sulphite liquor, only the phenolic compounds-phenol and guaicol- are likely to pose serious water quality problems as toxic substances. High concentrations of these compounds, particularly sugars, could produce O_2 -depleted waters which could represent a significant impairment of water quality. Additional analysis are required to identify other specific organics which may be of concern.

CONCLUSIONS AND RECOMMENDATIONS

At the present time large volumes of liquids (136 million liters in 1983) are applied to unpaved roads in Ontario for dust suppression. Although concerns regarding the fate and environmental consequences of the chemicals contained in these liquids have been expressed, thorough and comprehensive investigations have not been undertaken. Although the purpose of this particular study was to examine the potential for dust suppression practices to contribute to groundwater contamination, the results remain quite uncertain as a result of insufficient or incomplete background information. Additional information that would be particularly useful would include a complete inorganic and organic analysis of the various dust suppressant materials, and results of site-specific investigations.

Of the dust suppressants currently being used in Ontario, used oil appears to have the greatest potential to have adverse environmental effects. Although its use as a dust suppressant is declining, it is still used quite extensively in some parts of the province, and possible effects of previous applications should also be considered.

The composition of used oil is very complex, having characteristics associated with the original oil and also with its use. The composition is also extremely variable, depending upon the source of the oil. Used oil contains a wide range of both organic and inorganic "priority pollutants" and in many cases these occur at concentrations well in excess of recommended drinking-water limits. However, in the case of the inorganic constituents, because of dilution and geochemical retardation processes, it is unlikely that these will have a negative effect on local groundwater quality. In that the fate of organic materials in the environment is not well understood, the potential for groundwater contamination by organic constituents of used oil remains very uncertain. In that the drinking water limits for many trace organics are in the parts per billion or tens of parts per billion range, small quantities of organic materials can contaminate large volumes of water. It is therefore important that we be particularly vigilent with regard to these materials. More analyses of waste oils used in Ontario should be conducted, particularly with regard to the trace organic and heavy metal parameters. In addition, site-specific studies should be undertaken to determine if past practices have had an influence on the local soil and groundwater environments.

Calcium chloride is the most widely used dust suppressant, and appears to be increasing its share of the market at the expense of used oil. This should be an environmentally favourable trend in that calcium chloride has a very consistent composition and is not believed to contain significant concentrations of "priority pollutants". In that all soils and groundwaters of Ontario contain large amounts of calcium, that added by calcium chloride used for dust suppression would not cause a perceptible change. Chloride is highly mobile in soil-water and groundwater systems, and increases in chloride concentration in groundwaters adjacent to roads treated with calcium chloride could be expected. However, because of the high recommended drinking water limit for chloride (250 mg/l) it is unlikely that unacceptable concentrations would occur in the groundwater, or if they did, that they would persist beyond the immediate vicinity of the road.

Although calcium chloride is reported to contain only calcium chloride, there are undoubtedly other elements present in trace concentrations. It is unlikely that there occur at environmentally significant concentrations; however, a complete analysis should be undertaken.

The use of salt brine as a dust suppressant is increasing, particularly in south-western Ontario. The presence of chloride and calcium, and the high ionic strengths of the brines result in environmental consequences similar to those suggested for calcium chloride. In addition, because the brines are natural fluids and are extracted from different locations in different geologic formations, their composition is quite variable, and thus the environmental consequences are less predictable. In order to characterize the solutions, or to determine the range in characteristics, additional complete inorganic analyses should be conducted. No organic analyses of salt brines were found. In that the brines are derived from oil- and gas-yielding formations, it is reasonable to expect them to contain organic constituents, and therefore analyses should be conducted for these materials.

Because of its very limited use, sulphite liquor has a low potential to cause wide-spread degradation of the environment. Nevertheless, although little documentation is available, adverse effects are possible. In particular, the highly biodegradable nature of the organic fraction could lead to reducing conditions in aquifer materials, which could affect the mobility of other constituents, and phenol, one of the breakdown products of lignin is a recognized contaminant. From the analytical results that are available, sulphite liquor does not appear to contain specific parameters that are of environmental concern. It is recommended however, that complete organic and inorganic analyses of the liquor be undertaken.

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Table 1. Volume of suppressants applied in 1983

SOUTHERN ONTARIO COUNTIES	VOLUME (Litres)			
	Calcium Chloride	Used Oil	Brine	Sulphite Liquor
Brant	1,424,413	66,376		
Bruce	4,167,166			
Dufferin	2,469,993			
Dundas-Stormont-Glengarry	4,309,608			
Durham	4,091,400	1,775,494		
Elgin	1,159,230		7,773,500	
Essex	3,198,868		1,141,046	
Frontenac	1,742,633	318,220		
Grey	4,803,606	72,000		
Haldimand-Norfolk	2,273,000			
Haliburton	172,748	675,504		
Halton	578,826	365,528		
Hamilton-Wentworth	1,174,383	204,470		
Hastings	2,863,980	36,368		
Huron	5,727,960		477,330	
Kent	3,535,272		636,440	
Lambton	3,545,880		2,647,112	
Lanark	1,939,626			
Leeds and Grenville	3,126,132			
Lennox-Addington	925,868	1,710,800		
Manitoulin				
Middlesex	3,454,960		4,849,838	
Muskoka	780,396	1,291,230		
Niagara	2,803,366			
Nipissing				
Northumberland	939,506	1,188,860		
Ottawa-Carlton	3,106,433			
Oxford	4,294,454		3,091,280	
Parry Sound		1,952,634		
Peel	2,779,121			
Perth	3,712,566			
Peterborough	2,551,821	878,542		
Prescott-Russell	1,800,216			
Prince Edward				1,450,000
Renfrew	1,682,020			
Simcoe	3,838,339	3,729,167		
Toronto	297,005			
Victoria	3,265,543			
Waterloo	2,159,350	1,027,300	727,360	
Wellington	4,962,716			
York	1,772,940			
TOTAL	98,564,856	15,292,493	21,344,066	1,450,000
% of Total	72	12	15	1

Table 2. Length of road treated by various suppressants

SUPPRESSANT	TOTAL VOLUME (litres)	MEAN APPLICATION RATE (l/Km/year)	ROAD LENGTH (Km)	% OF TOTAL Km
Calcium chloride	98,564,856	3,724	26,463	89
Used oil	17,500,000	8,890	1,968	6.6
Brine	21,344,066	17,280	1,235	4.2
Sulphite liquor	1,450,000	16,948	8.5	0.003
TOTAL			29,751	

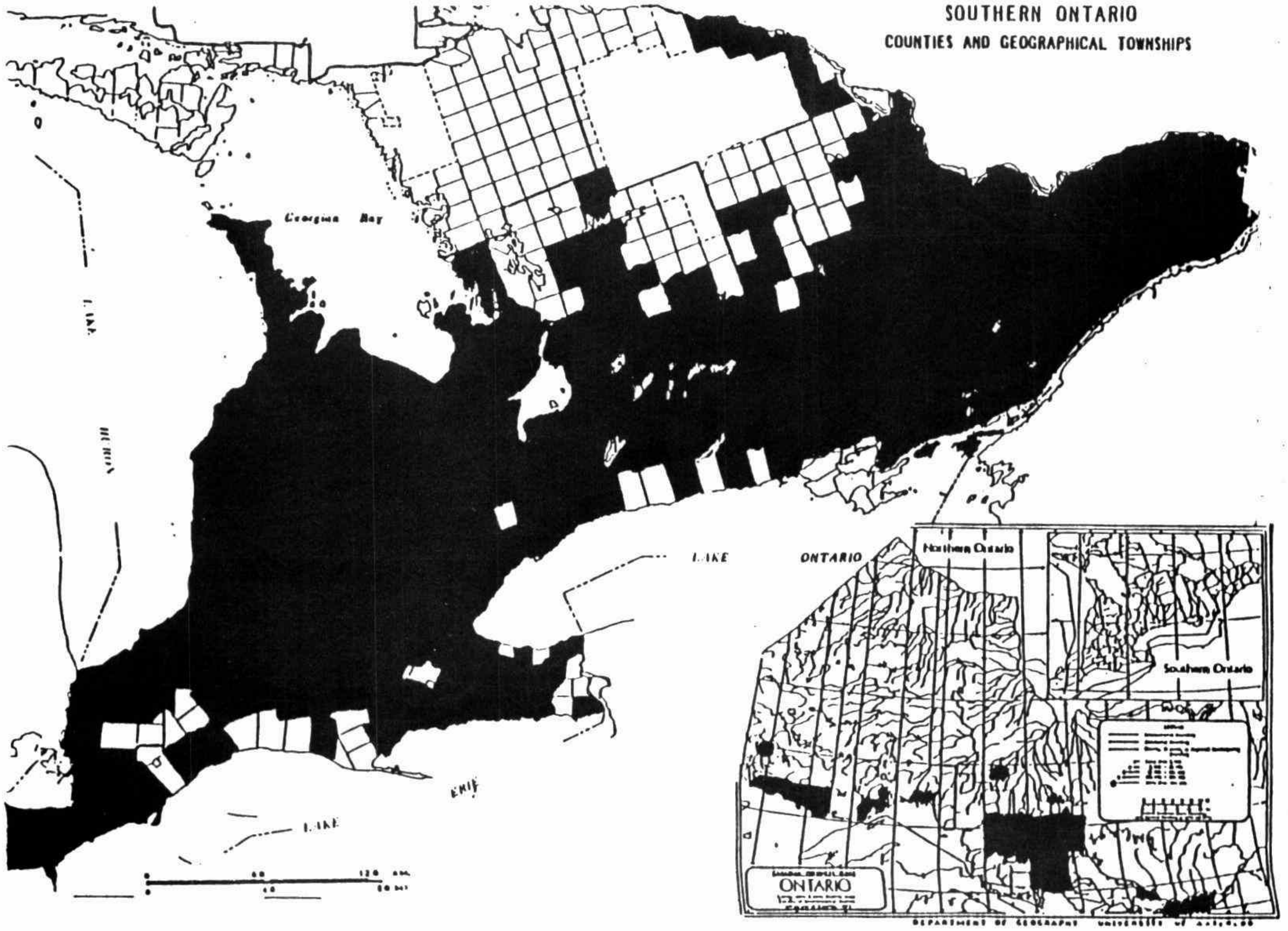

Figure 1. Distribution by township of use of calcium chloride for dust suppression in Ontario (1983)

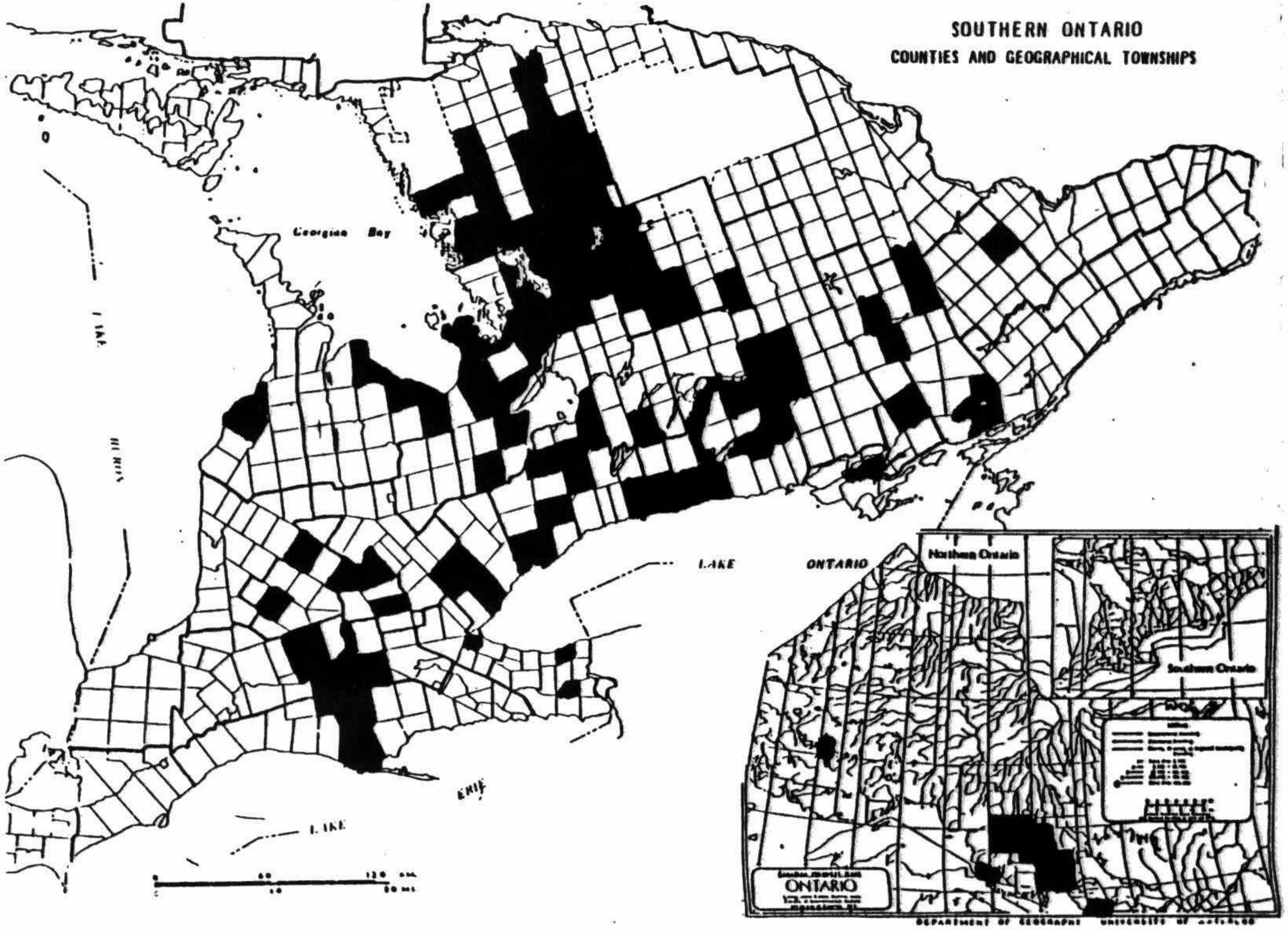

Figure 2. Distribution by township of use of used oil for dust suppression in Ontario (1983)

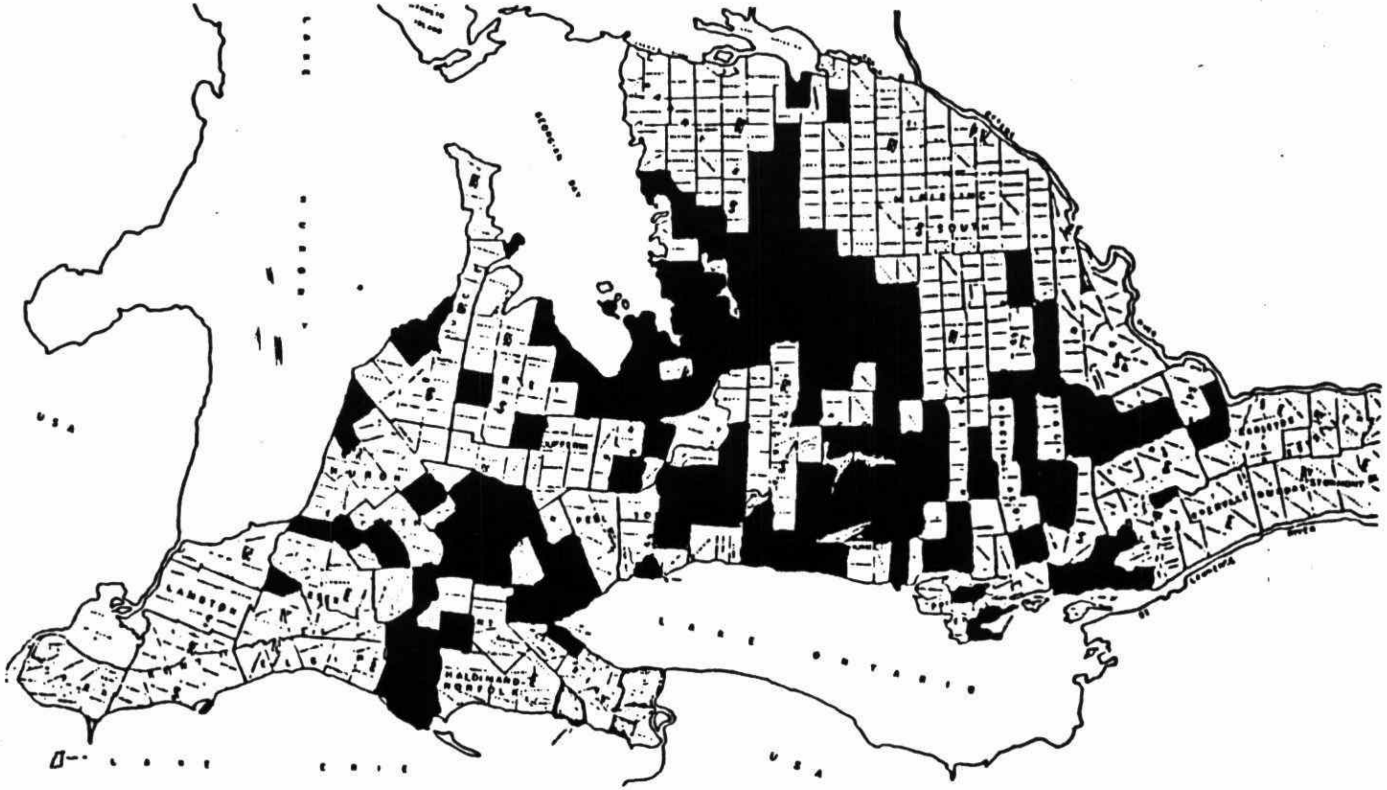

Figure 3. Townships using road oil as a dust suppressant during the period 1973 to 1978 (Ontario Road Oilers Association (1979))

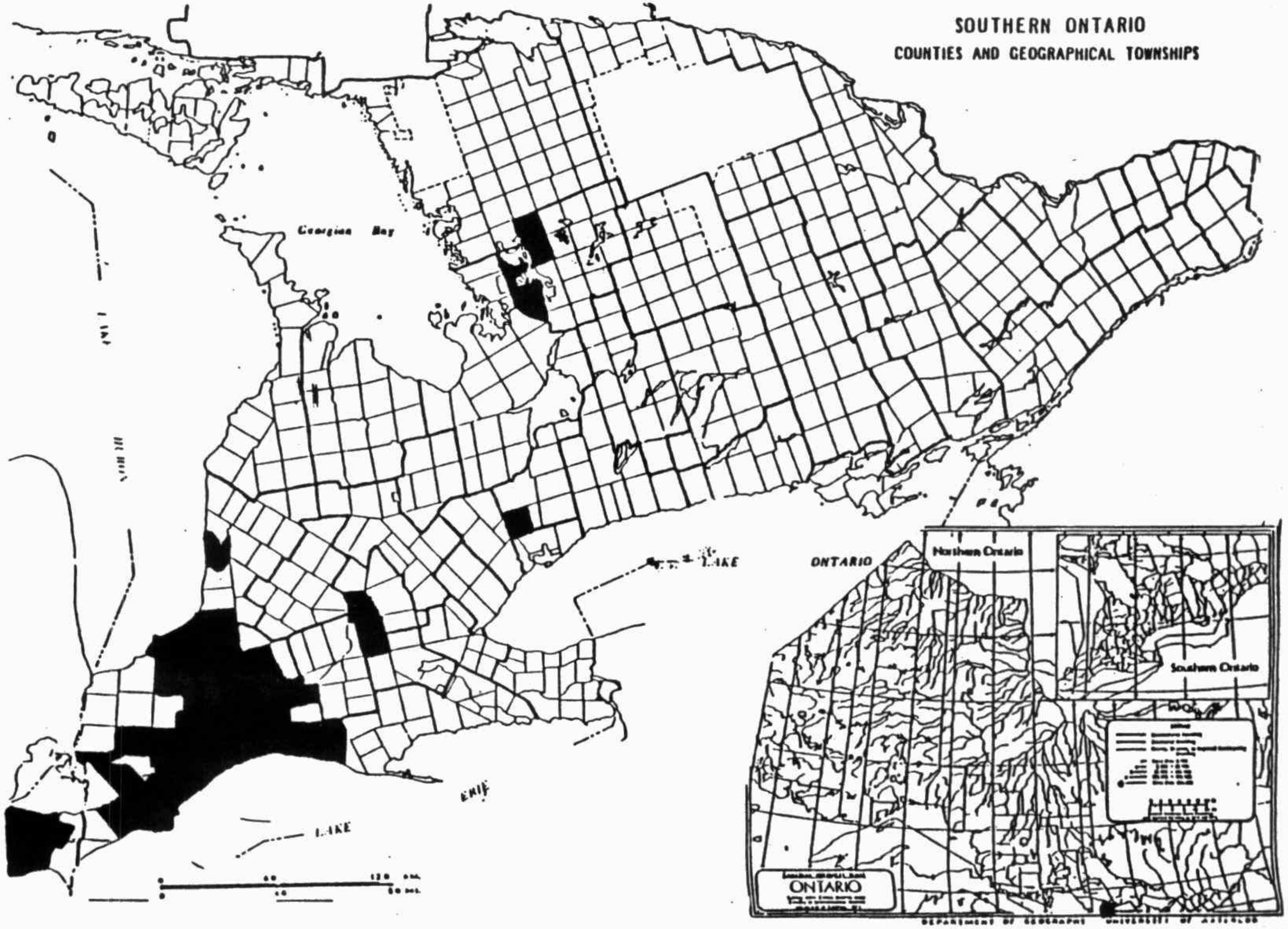

Figure 4. Distribution by township of use of salt brine for dust suppression in Ontario (1983)

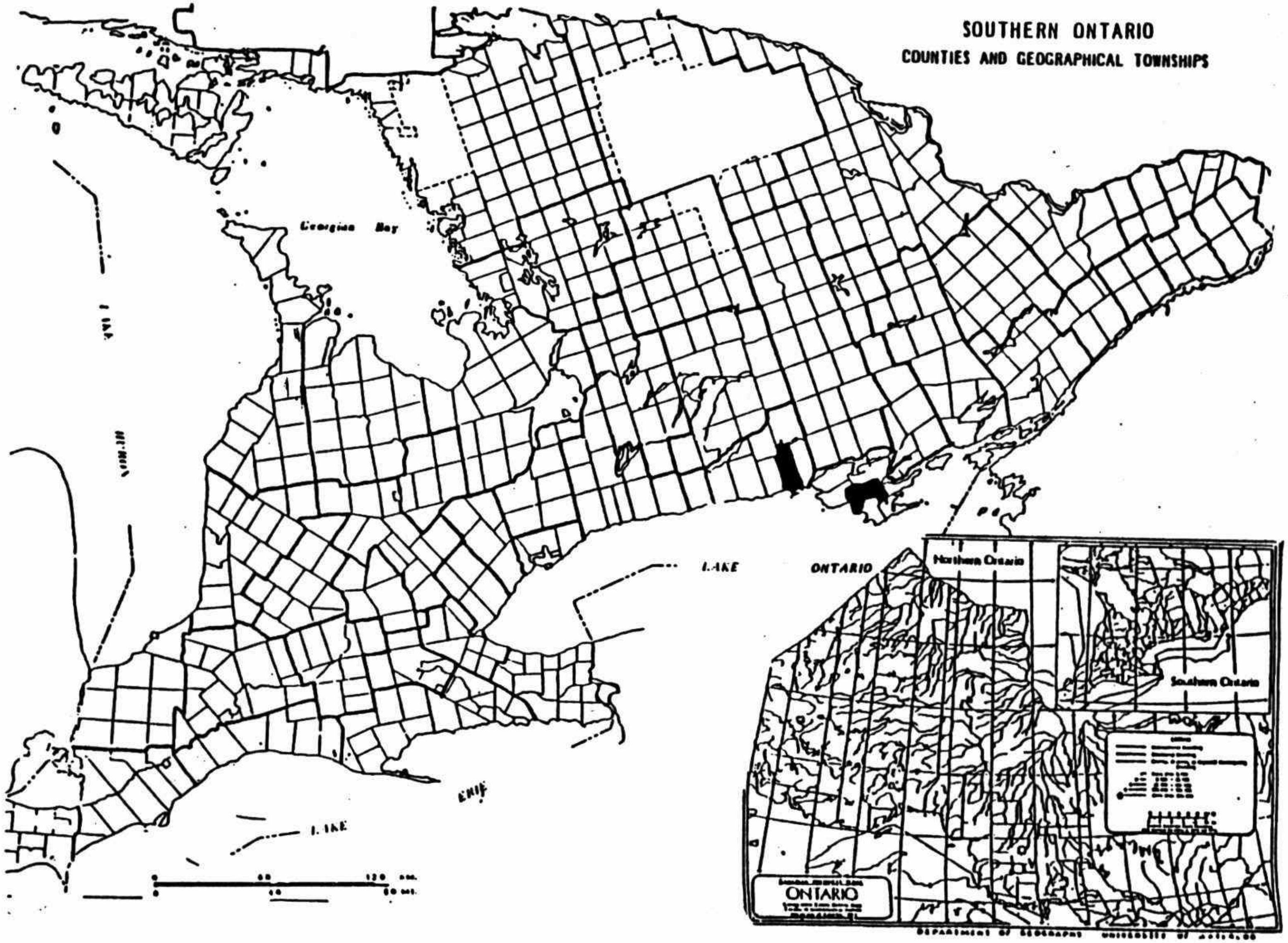

Figure 5. Distribution by township of use of sulphite liquor for dust suppression in Ontario (1983)

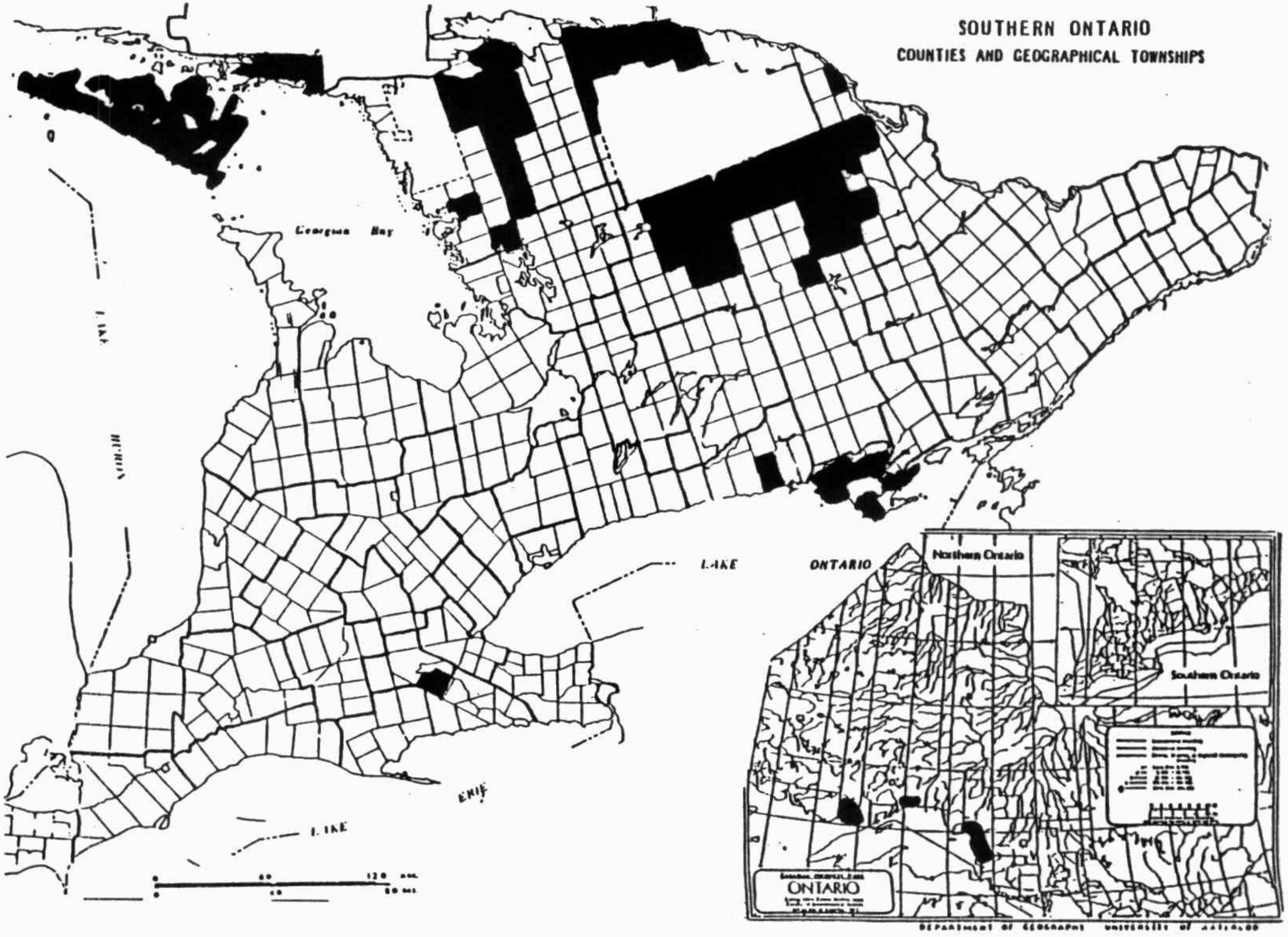

Figure 6. Townships for which no dust suppressant data was available

Table 3. Inorganic constituents of the major dust suppressant materials

Element	CONCENTRATION (mg/l) Used Automotive Oils[1] Range	 # Samples	 Used Industrial Oils[1] Range	 # Samples	 Salt Brine[2] Range	 #Samples	 Sulphite Liquor[3] Range	 # Samples	 Calcium Sulphide[4] Range	 # Samples
Al	0.4 - 800	28	2 - 36	2	- -	-	-	- -		
Ba	9 - 2,000	21	5 - 220	2	3 3	3	-	- -		
Be*	< .01 - 2.4	12	- -	-	- -	-	-	- -		
B	3 - 20	2	- -	-	77 - 108	3	-	- -		
Br	- -	-	- -	-	587 - 3,220	3	-	- -		
Cd*	.06 - 2.3	16	1 - 8	2	- -	-	.0001 -.001	U.K.		
Ca	270 - 3,000	22	- -	-	8,200-206,300	5	-	- -	166,482	all
Cr*	.03 - 60	10	1 - 31	2	- -	-	.001 - .05	U.K.		
Cl	- -	-	- -	-	161,200-403,207	5	-	- -	294,400	all
Co	- -	-	- -	-	- -	-	-	- -		
Cu*	5 - 348	27	3 1,160	2	- -	-	.001 - .03	U.K.		
Fe	40 - 2,000	29	1 200	2	- -	-	-	- -		
K	- -	-	- -	-	2,600 - 5,000	3	-	- -		
Pb*	< 10 21,700	29	0 -1,400	2	- -	-	.001 - .03	U.K.		
Mg	8 1,600	26	0 -1,000	2	2,850 -16,600	5	-	- -		
Mn	1 60	8	1 - 124	2	- -	-	-	- -		
Mo	1.4 50	6	0 - 19	2	- -	-	-	- -		
Hg	- -	-	- -	-	- -	-	<.0001 - .0003	U.K.		
Ni*	.34 50	16	0 - 27	2	- -	-	<.003 - .025	U.K.		
P	500 - 2,000	15	- -	-	- -	-	-	- -		
Se*	< .3 - <1.	2	- -	-	- -	-	<.01 - .03	U.K.		
Si	8 - 530	15	1 - 63	2	- -	-	-	- -		
Ag*	.01 - < 10	5	0 - .1	2	- -	-	<.0002 - .0008	U.K.		
Na	8 - 660	27	1 - 370	2	21-100,000	5	-	- -		
Sr	0 - 30	3	- -	-	214 - 1,620	3	-	- -		
SO_4	- -	-	- -	-	0 - 750	5	-	- -		
S	3,362 - 4,325	10	- -	-	- -	-	-	- -		
Sn	0 - 112	16	1 - 40	2	- -	-	-	- -		
Ti	< .01 - 30	4	0 - 7	2	- -	-	-	- -		
V	< .07 - 140	27	0 - 25	2	- -	-	-	- -		
Zn*	< 10 - 3,000	1,025	6 -1,100	2	- -	-	.003 - .1	U.K.		

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2. Fletcher, G.E., 1974
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Milne, 1983

3. Domtar Packaging Ltd., 1977
Fisher, R.P., 1979
Wong, A., 1982

4. (calculated)

* EPA Priority pollutants

U.K. - Unknown

Table 4. **Typical waste oil composition**

Group	Average Weight Percent
1. Normal and branched alkanes	27
2. Cyclic alkanes	50
3. Monoaromatic hydrocarbons	13
4. Polycyclic aromatic hydrocarbons	6
5. Heterocyclics	4
6. Halogenated hydrocarbons	¢ 1

Modified from reference 1.

Table 5. **Ranking of waste oil organics in terms of greatest theoretical concentration in associated water**

Organic	Theoretical Concentration in Water, $C_{i(H_2O)}$ (mg/l)	Ranking
1,1,2-Trichloroethane	18.5	1
1,1,1-Trichloroethane	2.9	2
Toluene	1.2	3
Trichlorofluoromethane	1.07	4
1,1,2-Trichloroethane	0.77	5
Trichloroethylene	0.72	6
Benzene	0.50	7
iso-Hexane	0.39	8
1,1,1-Trichloroethane	0.30	9
Propyl benzene	0.14	10
1-Methly 3-ethyl benzene	0.14	11
1 Chlorodifluoromethane	0.14	12
Xylenes	0.10	13
Cyclohexane	0.099	14
n-Hexane	0.09	15
Trichlorofluoromethane	0.069	16
Benzothiophene	0.057	17
Tetrachloroethylene	0.056	18
Cycloheptane	0.039	19
Naphthalene	0.029	20
n-Pentane	0.025	21
Diphenylmethane	0.014	22

CODISPOSAL OF INDUSTRIAL AND MUNICIPAL WASTES

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Key words: Industrial Wastes, Municipal Wastes, Waste Disposal, Landfill, Codisposal.

ABSTRACT

The use of municipal landfill sites for disposal of certain industrial wastes is very attractive because of the availability of disposal sites and relatively low disposal costs. The absorption of heavy metals from electroplating sludges by municipal refuse would appear to support the use of codisposal practice. However, the effects of the combination of industrial and municipal wastes on a long-term basis are not well established.

This project was undertaken to investigate the factors affecting the stability of industrial wastes in a simulated municipal landfill environment. Moderately large leach columns under both environmental and controlled conditions have been set up. A discussion will be given of the short-term laboratory leach test results and the long-term leach column experiments.

Co-disposal of Industrial and Municipal Wastes

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Abstract

The use of municipal landfill sites for disposal of certain industrial wastes is very attractive because of the availability of disposal sites and relatively low disposal costs. The absorption of heavy metals from electroplating sludges by municipal refuse would appear to support the use of codisposal practice. However, the effects of the combination of industrial and municipal wastes on a long term basis, is not well established.

This project was undertaken to investigate the factors affecting the stability of industrial wastes in a simulated municipal landfill environment. Moderately large leach columns under both environmental and controlled conditions have been set up. A discussion will be given of the short term laboratory leach test results and the long term leach column experiments.

INTRODUCTION

Landfill is the most common method of disposal for solid wastes. Typically sanitary landfill sites have been designated for municipal refuse and secure land fill sites for hazardous industrial wastes. However in recent years the regulation of secure land fill sites has become much stricter and it is apparent that there are relatively few sites that are environmentally or publicly acceptable. Thus judicous use of these sites is required.

Sanitary land fill sites have traditionally received varying quantities of hazardous wastes yet the impact on these sites is not understood. There may be certain industrial wastes that could be more appropriately disposed in sanitary land fill sites but the effects of codisposal must first be understood. The combination of municipal and industrial wastes must be viewed for both short and long term consequences. Short term effects are most easily studied but long term effects are of the greatest importance. Both aspects have been considered in this work.

Short Term Studies

The short term studies refer to laboratory experiments carried out under controlled, well defined conditions. The time frame is short relative to the simulated land fill tests and includes experiments of several months duration. The objectives in these studies are: to identify the effects of the combination of municipal and industrial wastes on standard classification tests, to identify the parameters having the most significance for long term predictive tests, and to identify the mechanisms involved in leachate formation in the co-disposal situation. Clearly it is important to establish whether short term leach tests leach tests have relevance in classifying wastes being considered for co-disposal with municipal refuse. The details of the tests will be described in the experimental section.

Long Term Studies

Long term consequences of co-disposal are most appropriately studied in actual land fill conditions. Unfortunately studies under field conditions present considerable experimental difficulty without the opportunity to resolve the underlying leachate formation mechanisms. The approach taken in this work was to construct a series of moderate sized leaching columns (13" diam. x 76") that could be exposed to the environment land fill conditions and permit comparison with identical columns having certain imposed conditions.

The long term effects of co-disposal are not simple functions of time, since the nature of a land fill undergoes distinct transitions. Five phases have been identified[1]. The initial phase occurs with the placement of the waste, subsidence, moisture accumulation and closure of the land fill area. The second phase is the transition to field capacity where leachate first appears and the conditions begin to shift to anerobic. The third phase shows organic acid production with a corresponding pH decrease and potential metal complexation and mobilization. The fourth phase is characterized by methane formation with pH controlled by bicarbonate. The organic content of the leachate decreases due to conversion to methane and carbon dioxide. The final phase is characterized by a cessation of gas production and a trend toward more aerobic conditions Humic acids tend to be produced in this phase which are capable of complexing and remobilizing heavy metals.

Clearly the stability of the industrial waste may be affected as the land fill conditions change and it is important to establish the significance of mobilization during each phase. In addition there is evidence[2] that municipal refuse has a capacity to absorb and inhibit migration of certain metal ions so that initial metal mobilization cannot be studied in isolation. The details of the long term tests are described in the experimental section.

The bulk of this paper will deal with the short term leach test results.

EXPERIMENTAL SECTION

Short Term Studies

Standard 24 hours leach tests were conducted using EPA EP extraction method using 0.5N acetic acid. The MOE variation of using 50 grams of solid in a rotating 30 rpm 1L vessel was followed. The final liquid to solid ratio was 20:1. The effect of the combination of industrial with municipal refuse was tested. The four levels of industrial waste in the 50 g sample were 0, 4, 15 and 50 grams. The method of pH adjustment followed the EPA procedure using acetic acid. Alternative solvents tested were deionized water, aqueous sulphur dioxide and municipal refuse leachate. In the case of aqueous sulphur dioxide the molar equivalent of acetic acid was used. After the leaching period the leachates were filtered and acidified with nitric acid acid for ICP analysis. It was found that acidification was best performed shortly before analysis otherwise precipitation was found. Additional analysis were performed by NAA at the McMaster Reactor to cross check and extend the range of elements measured. For ICP the elements Mg, Al, V, Cr, Mn, Fe, Ni, Ca, Zn, Co and Pb were analyzed. For NAA Br, Mg, Cu, Na, V, K, Cl, Al, Mn and Ca were analyzed. Duplicate standards were run for each analysis. Longer leaching times were tested though not under the continuous rotating conditions of the 24 hour test. Samples of the municipal refuse with the various levels of industrial wastes used in the 24 h tests were placed in polyethylene bags with the four specified solutions. For the acetic acid, the EPA acid addition procedure was followed. For the aqueous sulphur dioxide the molar equivalent to the acetic acid was used. No additions were made to the deionized water or municipal leachate. Mixing was achieved by manually squeezing the bags every few days. Both one week and one month leach test were analyzed. These tests did not breakdown the structure of the municipal refuse to the same extent, as did the 24 hour continuous rotating action.

The municipal leachate, was prepared by recirculating 20.7 kg of deionized water through a bed (9.95 kg dry wt) of municipal refuse for a period of 3 weeks. This solution which had a pH of 7.89 was used in the leaching tests after filtration.

Long Term Leach Tests

The details of a leaching column is shown in Figure 1. The municipal refuse used in the leaching columns and in the short term leach tests was potentially treated. The refuse was shredded to pass a 4 inch sieve. Both fall and summer refuse was blended before packing in the columns. The manual packing achieved an average density of 631 kg/m^3 wet weight basis and 291 kg/m^3 dry weight basis. Additional settling of 5 cm per 1.8 m depth was observed within the first two months. Characterization of the refuse provided by the Ontario Centre for Resource Recovering is shown in Table 1. The values are typical of municipal refuse.

Distilled water is added to the control columns at the average monthly by rainfall rate. Leachate was found at the bottom of some of the columns within two weeks of packing completion.

Leach Column Experiments

A total of 16 columns were prepared having 8 variations and 8 replicates. The levels of industrial waste were 0%, 8% and 30% of municipal refuse dry weight. The 8% weight of industrial waste also was packed in a sand leaching column. A duplicate of each column was prepared for each test condition to permit comparison of both atmospheric and controlled water additions.

The industrial waste (a flue gas dust from a steel plant) was put into three layers to simulate land fill usage and the layers were spaced in the columns as shown in Figure 1. Five sample ports plus a bottom drain allowed samples to be withdrawn and analysed for metal migration and leachate formation.

RESULTS

Table 1 shows the municipal refuse characterization as given by the Ontario Centre for Resource Recovery. Moisture and paper constitute the bulk of the refuse. A sample of the industrial waste was analyzed by XRF with the results given in Table 2. A chemical analysis of the solid was performed using NAA shown in Table 3. Short, medium and long lived isotopes were measured. ICP analysis was used for a sample digested in aqua regia with and without hydro fluorc acid. These results are shown in Table 4. As would be expected the use of hydroflouric acid does increase the level of metals dissolved but the increase is significant only in the case of aluminum (from silicate dissolution) and copper. There are significant differences between ICP and NAA analysis for iron, zinc and calcium. The other elements recorded are fractionally higher in NAA analysis since the solid and not the dissolved fraction are analyzed. The discrepancy between the two methods for iron, zinc and calcium is not easy to explain since consistent values were obtained with each method. Investigation of the cause of the discrepanies will be carried out. It should be noted that the ICP values will probably better reflect the maximum metal content that could be leached in a land fill environment. Manganese, lead chromium and cadmium will consitute the metals of environmental concern.

The standard 24 hour EP leach test with acetic acid was carried out using the municipal refuse and industrial waste alone and in combination. The resulting solutions were analyzed by both ICP and NAA and the values are shown in Table 5 a and b. It should be noted that the elements Mn, Mg, Al, and Cu could be determined by both NAA and ICP. There is very good correlation between ICP and NAA analysis as shown in Figure 2. There is however a difference in the relative magnitudes of magnesium concentration determined by ICP and NAA. Magnesium concentrations are a factor of almost 1.5 higher by ICP analyses than NAA analyses. The reason for this difference is not known. Despite the difference and scatter of the data a correlation coefficient of 0.97 was determined for the comparison indicating self consistency for each technique.

From the 24 hour leach test of the municipal refuse alone there are relatively low levels of metals leached. Surprisingly manganese was found at about 3.5 ppm, approximately the same concentration as iron. With the mixed samples of municipal refuse and 8% industrial waste (4g in 50 g) higher levels of all metals were found indicating dissolution of some of the industrial waste. In particular zinc, lead, cadmium and manganese were found to be substantially elevated. At this level of industrial waste, the leachate can be titrated to a pH of 5.3 without exceeding the specified maximum acetic acid addition.

With 30% by weight industrial waste in the leach test sample, the pH cannot be held to a value of 5 even with the maximum specified acetic acid addition. For this test the resulting pH was 6.6. The higher pH apparently inhibited iron but did not prevent lead, manganese, or calcium from dissolving. For a sample which had only industrial waste the pH remained very alkaline (11.9) even after addition of 200 ml of 0.5 N acetic acid. This high alkalinity inhibited most of the metals for dissolving with the exception of lead chromium and calcium. The lead level was found to be $\sim$ 175 ppm. The solubility may be due to the presence of $Pb\,O_2^-$ which is stable in very alkaline conditions. Thus one might anticipate mobilization of lead in the industrial waste layer but precipitation in the municipal refuse environment. Chromium concentrations reached 0.45 ppm and also appeared to have a greater solubility under the alkaline conditions. The level of calcium appears to reach the saturation level predicted by acetic acid addition. This aspect is important since in a land fill the calcium will eventually be leached allowing the pH to decrease and metals to be solubilized.

The 24 hour test was repeated using deionized water and the results are shown in Table 6. There is little difference in the results in leaching the municipal refuse alone. However with the industrial waste added to the municipal refuse the pH of the solution was found to be more alkaline due to the calcium oxide in the waste. Thus the level of metals leached were lower than found with the acetic acid treatment. A notable exception was that lead leached more freely from the pure industrial waste sample (240 ppm). It is clear that as the buffering capacity of the leachate is reduced the amount of lead solubilization is increased. The pH of the leachate appears to correlate the formation of calcium hydroxide.

The same 24 hour test was repeated with aqueous sulphur dioxide using molar equivalents of the acetic acid test. These results are shown in Table 7. In general the levels of metals leached appear to the same as for deionized water if the pH of the solution is taken into account. One exception is manganese which is more readily solubilized by the aqueous sulphur dioxide than deionized water however these levels also were achieved using the acetic acid leach. Thus aqueous sulphur dioxide as might be found in acid rain, does not appear to present any increased metal complexation that wouldn't be found using acetic acid. Both electrolytes however, by providing buffering capacity do not predict the very high lead solubilization observed with deionized water.

A solution was generated from recirculating deionized water through municipal refuse as described earlier. This solution was used as a leachate in the 24 hour test to compare its metal solubilization ability with the other leachates. The use of municipal refuse leachate has been studied to identify the mobility of certain toxic species at the Oak Ridge National Laboratory by Maskarinec and Francis. Since the leachate has had an opportunity to solubilize various organics and metal ions one might anticpate higher metal loadings than found with the simple deionized water leach (Table 6). The results shown in Table 8, indicate that little if any additional metal solubilization occurs. Only magnesium increases in the expected manner. Thus it appears that the metal concentrations found in the deionized leachate test of municipal refuse are at a saturation level. More over the presence of 8% industrial waste in the test sample (R 14A and R14B) results in a decrease in the metals Mn, Mg, Fe, and Ni. Undoubtedly the rise in pH from 6.9 to 9.2 due to the alkaline nature of the industrial waste is the primary cause of the concentration drop of these metals. One consequence of this effect is that a layer of industrial waste in a land fill site may accumulate certain metals through precipitation of migrating ions.

The municipal refuse leachate has some buffering capacity with the pH reaching 9.2 with 8% I.W. in the sample compared to 10.75 for the identical test with deionized water. This buffering capacity has the effect of slightly reducing the solubilization of lead.

One of the concerns about the 24 hour leach test is that the conditions do not reflect the anaerobic conditions which generally exist in the land fill environment. In addition there is insufficient time to develop microbial action which may induce metal mobilization. For this reason laboratory tests were carried out for a one week and a one month period to allow the observation of changes in the leaching characteristics.

Table 9 shows the data for a one week acetic acid leach test. The longer leach period caused slight increases in the amount of Mn, Mg, Cr, Ni, Pb, Ca, Br, Cl, V, and Na, typically about 10-20%. However the ion concentration rose from ~ 3.7 to 47.3 ppm. With 8% industrial waste in the sample, the week long leach showed higher Mn, Cr, Fe, Ni, Cl, V, Na, and K.

The 100% industrial waste sample using a one week leach compared to the 24 hour leach did not show any major variations of leaching extent but this result is due to the very high pH levels of the test. The leach test under these conditions is simply a chemical process whereas at lower pH values in the mixed samples biological activity was observed.

The one month leach test results (Table 10) show that of the metals measured only Mn and Fe were at higher levels than found in the 24 hour and 1 week tests. Other metals such as Mg, Al, Cu, Cr, Ni, and Zn had lower values than 1 week test results, and Al, Cu, and Zn were lower than the 24 hour test results. Thus it appears that there is an exchange of metals in solution with iron and manganese slowly entering the solution while others such as Al, Cu and Zn precipitate. At this point it is not clear whether this process represents a common ion effect or a modification of the leachate through biological action and pH buffering .

With the pure industrial waste little difference is seen between the 24 hour and 1 month test because the high pH controls the leaching action with no evidence of biological activity.

The 1 week and 1 month tests were repeated using deionized water as the solvent. These results are shown in Tables 11 and 12. In general the amount of metals leached from the municipal refuse alone did not change from the 24 hour leach test despite the very obvious biological action during the 1 week and 1 month tests. The exceptions were Al and Zn which were depressed in the longer tests. The pH stabilized very close to the neutral point for the 1 week and 1 month tests.

With 8% I.W. in the sample the initial high pH observed in the 24 hour tests (10.75) was reduced at the end of 1 week to 10.15 and to 7.8 at the end of 1 month. This buffering action due to organic acid and carbon dioxide production resulted in a greater solubilization of Mn, Mg and Zn but a loss of Al, Cr, Fe, Cd and possibly Pb. The loss of Fe and increase of Mn were the reverse of the trends observed for the acetic acid leach tests. This variation points to the difference in the nature of the metal complexing action of the acetate ion and the anaerobic generated organic acids.

One week and one month tests involving 30% and 100% industrial waste did not reveal any substantial change from the 24 hour test with deionized water with the exception of a slight reduction in the lead solubilization. The reason for similarity of the two tests was that the high level of industrial waste inhibited biological action so that the pH remained very alkaline for the test periods.

It is interesting to compare the pH modification that results when municipal leachate is used as the leaching solution. The pH values for 1 week and 1 month tests are shown in Tables 13 and 14. The pH of the 30% I.W. sample was eventually buffered over a 1 month test period by the municipal refuse. It is likely therefore that with longer testing periods that 30% levels of I.W. could be buffered starting with only deionized water. Thus the presence of stabilized or very alakaline industrial wastes only temporarily inhibit biological action. The chemical nature of the buffering action appears to effect the mobilization of some metals. The tests R47A and R47B in Table 14 have pH levels 7.91 and 7.80, much lower than found at the end of the 1 week test (pH ~ 12). Despite the nearly neutral pH condition the metal concentration levels appear to be much closer to those found at pH 12 than 7.8. It would appear that the assimulation of metals does not take place immediately upon neutralization but may require the generation of excess organic species.

Also there is evidence that the municipal leachate has some ability in inhibiting Pb dissolution even under alkaline conditions. The one month leach tests (Table 14 R48A, B) indicate much lower lead levels (≃ 67 ppm) than would be predicted at those pH values (200 ppm) in deionized water leach tests.

Comparison of the EP Leach Test with Short Term Leach Tests.

The present EP tests using a maximum addition of 200 ml of 0.5 N acetic acid per 50 g of solid does not provide sufficient buffering for testing alkaline containing or alkaline stabilized industrial wastes. Thus the ratios of metal ion concentration found from 4 g of I.W. in 46 g municipal refuse compared to 50 of I.W. are 125 for Mn, 118 for Mg, 2.2 for Al, 1.46 for Cu, .23 for Cr, 64 for Fe, >67 for Ni, 0.5 for Zn, >46 for Cd, <0.05 for Pb. These values were obtained after substracting the municipal refuse metal ion contribution . It has been proposed to change the EP procedure to allow addition of more buffering capacity which would correct this discrepancy. However one consequences of this would be to reduce the mobilization of lead and chromium which occur under very very alkaline conditions. Whether the loss of information regarding lead and chromium is significant will depend on how mobile the ions remain in the land fill environment. It is anticipated that the initial phase in the simulation landfill conditions in the leaching columns will show the greatest degree of lead mobilization since calcium levels and hence pH will be high.

It should be noted that in all of these batch type tests the concentration of certain metal ions may be limited by solubility considerations. Calcium appears to be limited in the deionized water tests by the K_{sp} for $Ca(OH)_2$. The high loading of calcium may produce a common ion effect in a batch test, which would not be observed in a leach column. Certainly with the high solubility of calcium, continuous leaching will result in rapid loss of the alkalinity of the industrial waste allowing microbial action to begin. It will be necessary to use column measurements to determine the actual rate of migration of the various metals ions through the municipal refuse environment. These results will be reported in future work.

Conclusions

The standard EP leach test for solid wastes for co-disposal should be modified to allow greater buffering for testing alkaline wastes. When a lower solid waste to liquid ratio is used, the metal concentrations produced are higher than those found from leaching with deionized water, aqueous sulphur dioxide or synthetic municipal leachate with the exception of copper and aluminium. These methods while initially solubilized stabilize at lower concentrations during longer leach tests so that the under prediction does not appear to be a serious flaw.

Biological action in the longer tests demonstrated the neutralization of very alkaline solutions. The action was associated with increased metal solubilization but the concentrations did not exceed the levels indicated by an 8% I.W. EP test. In general the 8% I.W. test was a more satisfactory indicator of the concentration of metals leached by deionized water, aqueous sulphur dioxide or synthetic municipal leachate. Longer leach tests are required to follow the change of concentrations as the leachate composition changes.

Lead is very soluble in the industrial waste environment due to the very alkaline conditions and will be expected to migrate. The extent of migration in the municipal refuse environment must be determined.

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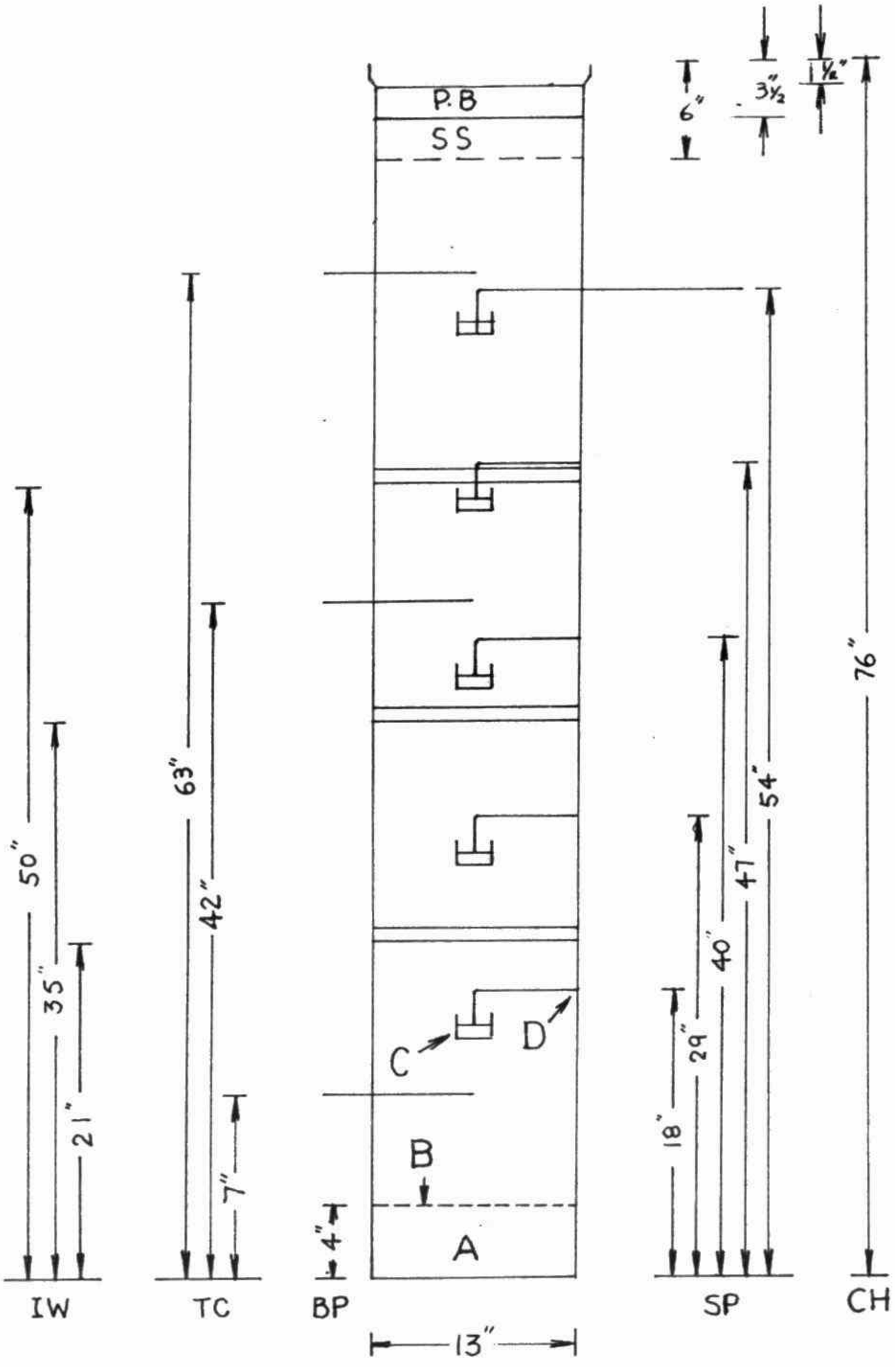
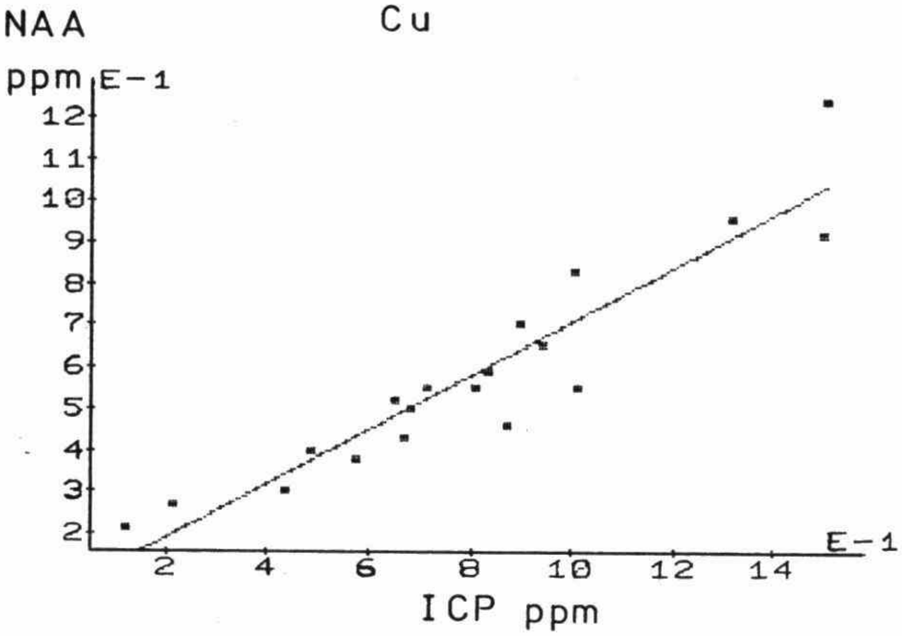


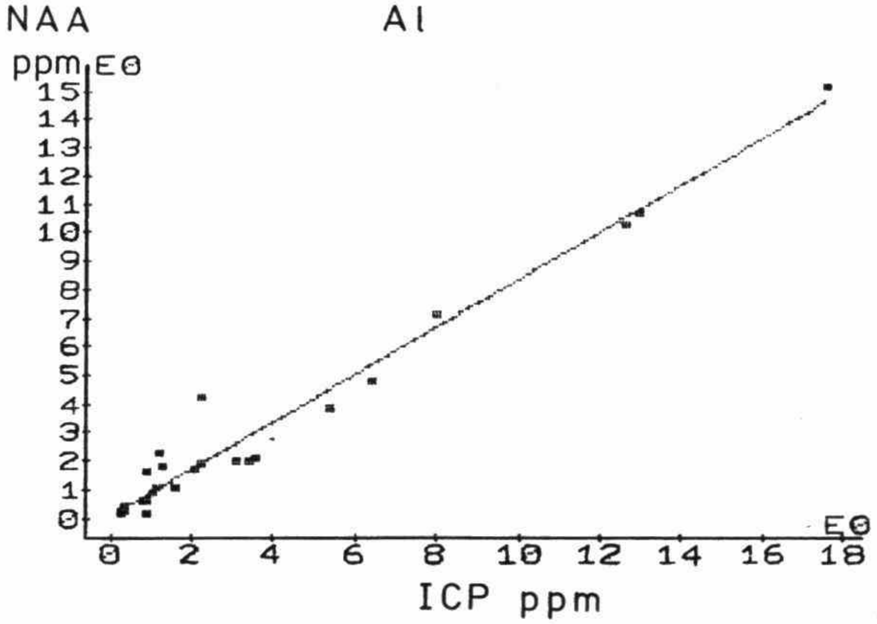
SCALE : 1" to 1'

IW	*Industrial Wastes*
TC	*Thermocouples*
BP	*Bottom Plate*
SS	*Silica Sand (20 Mesh)*
SP	*Sampling Ports*
PB	*Polypropylene Beads (1/8")*
CH	*Column Height*

Details of A, B, C, and D are shown in Fig 1(b) and Fig 1(c)

Fig. 1 Column Interior and Dimensions


NAA
ppm
E-1
Cu
12
11
10
9
8
7
6
5
4
3
2
2
4
6
8
10
12
14
E-1
ICP ppm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ppm
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Al
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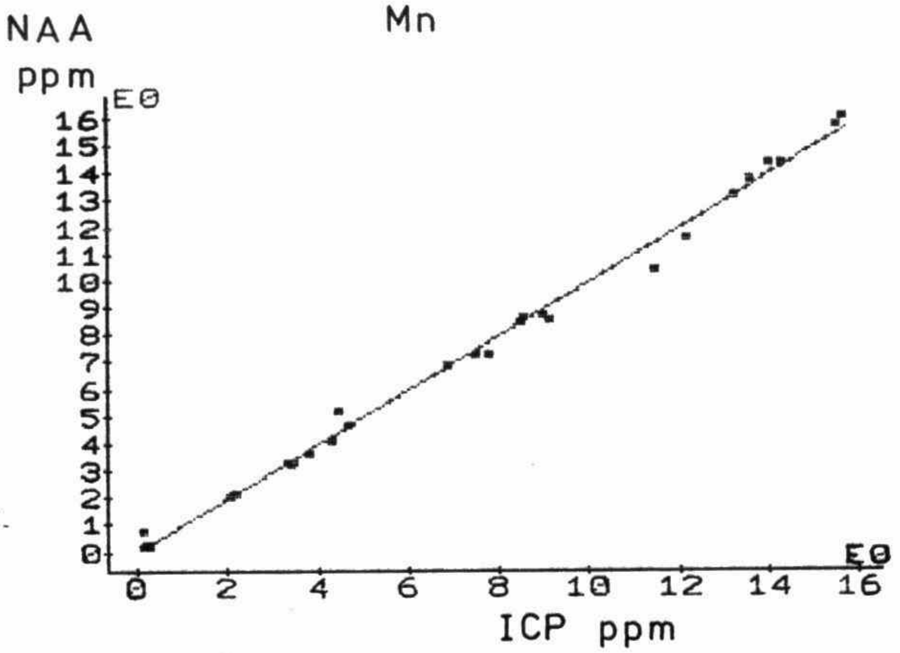
8
10
12
14
16
18
E0
ICP ppm

Fig 2a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ppm
Mn
E0
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15
14
13
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11
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E0
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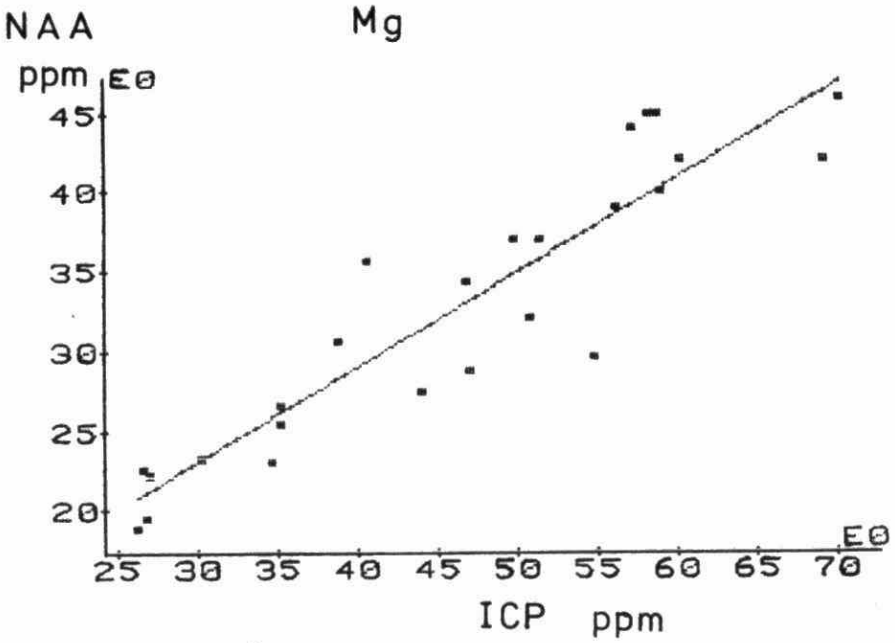
2
4
6
8
10
12
14
16
ICP ppm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ppm
Mg
E0
45
40
35
30
25
20
E0
25
30
35
40
45
50
55
60
65
70
ICP ppm

Fig 2b

Table 1

Municipal Refuse Characterization

Component Analysis (weight %)

	% moisture	Paper	Natural Organics	Synthetic Organics	Ferrous	Nonferrous	Glass	Fines
Fall Sample	27.2	54.0	0.8	7.2	10.1	1.5	1.2	24.9
Summer Sample	14.0	25.3	17.0	20.4	8.6	-	1.5	26.5

Percent Particle Size Retained

4"	2"	1"	½"	¼"	#8	Pan
0.4	40	23.8	25.6	20.4	14.9	10.6

Table 2

XRF Analysis of Industrial Waste

% Dry Weight

SiO_2	Al_2O_2	CaO	MgO	Na_2O	K_2O	Fe_2O_3	MnO	TiO_2	P_2O_5	Cr_2O_3
4.85	0.93	5.97	4.57	3.00	0.41	41.7	5.94	0.01	0.15	0.40

Table3a

Neutron Activation Analysis (NAA)

Industrial Solid Wastes (Steel Flue Dust)

Elements	Concentration (dry weight basis)
Br	231 ppm
Cu	3076 ppm
V	64 ppm
Na	1.03 %
Cl	2.44 %
Al	0.29 %
Mn	5.15 %
Ca	4.21 %

Table 3b

NAA for Medium-lived Elements of Industrial Solid Waste (Steel Flue Dust)

Elements	Concentration
Sm	0.07 ppm
Ce	12.6 ppm
Sc	0.51 ppm
Mo	46 ppm
As	99 ppm

Table 3c

NAA for Long-lived Elements of the Industrial Waste (Steel Flue Dust)

Elements	Concentration
Cr	2805 ppm
Sb	44 ppm
Co	22 ppm
Fe	40.0 %
Zn	9.4 %

Total = 62.52%

and 37.48% unaccounted (ie. oxides)

Table 4

Inductivity Coupled Plasma Spectroscopy (ICP) Analysis of the Industrial Solid Waste (Steel Flue Dust)

Aqua Regia Digestion		Aqua Regia with HF Digestion	
Element	% Dry Weight	Element	% Dry Weight
Fe	26.82	Fe	27.15
Zn	14.07	Zn	14.08
Ca	11.90	Ca	12.40
Mn	4.01	Mn	4.09
Pb	1.99	Pb	1.97
Cr	0.213	Cr	0.220
Al	0.205	Al	0.351
Cu	0.182	Cu	0.229
Ni	406 (ppm)	Ni	392 (ppm)
Cd	352 (ppm)	Cd	323 (ppm)
Co	30 (ppm)	Co	22.9 (ppm)

Table 5

Standard 24 Hour Leach Test
(ppm)

a) ICP Leachate Analysis

Sample	pH	Acid Addition (mL)	Amount of I.W. (g)	Mn	Mg	Al	Cu	Cr	Fe	Ni	Zn	Cd	Pb
R 9A	5.8	3.3	0	3.38	3.53	1.22	0.142	0.033	3.21	0.076	2.78	<0.016	<0.23
R 9B	5.8	3.3	35.3	3.30	3.53	2.20	0.364	0.040	4.16	0.104	4.06	<0.016	<0.23
R10A	5.2	104	4	7.79	44.0	1.60	0.58	0.096	6.23	0.196	>155	0.67	8.88
R10B	5.4	104	4	8.95	60.3	3.12	0.68	0.160	10.4	0.225	>155	0.80	8.68
R11A	6.6	200	15	7.49	4.97	0.30	0.94	0.041	1.04	0.150	>155	2.14	28.7
R11B	6.5	200	15	11.44	69.2	0.37	0.87	0.061	0.32	0.273	>155	2.75	54.5
R12A	11.8	200	50	0.06	0.55	0.30	0.31	0.253	0.12	<0.07	6.86	<0.016	196
R12B	12.0	200	50	0.02	0.32	0.30	0.23	0.637	0.016	<0.07	5.86	>0.016	153

b) NAA Leachate Analysis

Sample	pH	Acid Addition (mL)	Amount of I.W. (g)	Mn	Mg	Al	Cu	Cr	Fe	Ni	Zn	Cd	Pb
R 9A	5.8	3.3	0	3.25	26.6	2.31	-	324	0.271	110	.0065	100	78
R 9B	5.8	3.3	35.3	3.26	25.4	4.27	-	322	0.302	99.0	.0074	105	61
R10A	5.2	104	4	7.25	27.5	1.08	0.38	568	2.36	147	-	107	67
R10B	5.4	104	4	8.67	42.0	1.98	0.50	702	2.55	156	-	117	82
R11A	6.6	200	15	7.26	35.7	0.16	0.65	1269	7.07	230	-	125	94
R11B	6.5	200	15	10.4	42.0	0.24	0.46	1300	6.41	230	-	119	87
R12A	11.8	200	50	-	-	-	-	2368	24.1	719	-	257	240
R12B	12.0	200	50	-	-	-	-	2573	25.5	723	-	263	220

Table 6

24 Hour Leach with Deionized Water
ICP Leachate Analysis (ppm)

Sample	pH	Acid Addition	Amount of I.W. (g)	Mn	Mg	Al	Cu	Cr	Fe	Ni	Zn	Cd	Pb
R1A	6.7	-	0	2.08	26.9	4.25	0.14	0.043	6.83	0.070	1.11	<0.016	<0.23
R1B	6.6	-	0	1.72	33.5	1.25	0.75	0.062	7.31	0.109	2.14	<0.016	2.48
R2A	10.8	-	4	0.278	1.33	12.6	1.01	0.205	2.23	0.074	2.55	0.078	0.97
R2B	10.7	-	4	0.613	2.28	17.6	0.832	0.158	3.96	0.083	6.04	0.083	1.31
R3A	12.0	-	15	0.040	0.099	0.245	1.50	0.508	0.350	<0.07	2.29	<0.016	0.36
R3B	12.4	-	15	0.047	<0.07	0.852	1.01	0.412	0.065	<0.07	1.89	<0.016	0.35
R4A	12.2	-	50	0.002	0.150	0.144	0.110	0.137	0.017	<0.07	4.06	<0.016	257.2
R4B	12.5	-	50	0.002	0.144	0.151	0.103	0.149	0.013	<0.07	3.76	<0.016	225.6

NAA Leachate Analysis

Sample	pH	Acid Addition	Amount of I.W. (g)	Mn	Mg	Al	Cu	Cr	Fe	Ni	Zn	Cd	Pb
R1A	6.7	-	0	2.01	22.3	14.5	-	167	0.243	87.3	0.0224	87.4	48
R1B	6.6	-	0	2.0	22.3	14.5	-	167	0.243	87.3	0.0224	87.4	48
R2A	10.8	-	4	0.266	<	10.3	0.55	200	4.91	143	0.008	98.0	63
R2B	10.7	-	4	0.716	8.9	15.2	0.58	184	2.45	156	0.013	110	68
R3A	12.0	-	15	<	<	0.180	0.92	731	8.41	297	<	139	112
R3B	12.4	-	15	<	<	0.641	0.83	692	8.21	293	<	141	102
R4A	12.2	-	50	<	<	<	<	939	25.3	724	<	255	261
R4B	12.5	-	50	<	<	<	<	909	26.4	729	<	261	253

Table 7

24 Hour Leach with Aqueous Sulphur Dioxide
ICP Leachate Analysis (ppm)

Sample	pH	Acid Addition (ml)	Amount of I.W. (g)	Mn	Mg	Al	Cu	Cr	Fe	Ni	Zn	Cd	Pb
R5A	5.2	11	0	3.72	31.5	1.80	0.37	0.048	4.82	0.130	4.53	<0.016	<0.23
R5B	5.4	11	0	3.92	36.3	1.45	0.62	0.046	3.89	0.132	4.59	<0.011	<0.23
R6A	4.6	33	4	13.2	50.9	3.44	0.81	0.161	26.5	0.366	>155	0.43	1.48
R6B	4.4	37	4	12.2	54.9	3.55	0.90	10.186	27.7	0.470	>155	0.45	1.03
R7A	7.3	42	15	4.3	34.7	0.374	0.48	0.049	1.58	0.187	>155	0.25	8.16
R7B	6.4	50	15	9.1	47.1	0.793	0.65	0.098	2.20	1.53	>155	0.32	2.26
R8A	12.4	42	50	0.00	0.14	0.16	0.079	0.359	0.034	0.149	3.76	<0.016	112
R8B	12.1	50	50	0.006	0.12	0.16	0.065	0.444	0.617	<0.07	3.29	<0.016	96.0

NAA Leachate Analysis (ppm)

Sample	pH	Acid Addition	Amount of I.W. (g)	Mn	Mg	Al	Cu	Cr	Fe	Ni	Zn	Cd	Pb
R5A													
R5B													
R6A													
R6B													
R7A													
R7B													
R8A													
R8B													

Table 8

24 Hour Leach with Municipal Refuse Leachate
ICP Leachate Analysis (ppm)

Sample	pH	Acid Addition (ml)	Amount of I.W. (g)	Mn	Mg	Al	Cu	Cr	Fe	Ni	Zn	Cd	Pb
R13A	7.0	-	0	1.63	65.2	0.322	0.099	0.048	5.43	0.58	0.14	<0.016	<0.23
R13B	6.9	-	0	2.11	67.5	0.691	0.094	0.058	9.92	0.12	0.30	<0.016	<0.23
R14A	9.4	-	4	0.32	27.7	0.523	0.343	0.065	2.67	0.12	3.74	0.021	0.71
R14B	8.9	-	4	0.37	39.5	0.418	0.193	0.079	2.31	0.13	3.44	0.031	1.36
R15A	12.2	-	15	0.037	<0.068	1.573	1.849	0.381	0.48	<0.07	1.32	<0.016	4.04
R15B	12.3	-	15	0.028	0.112	0.649	1.247	0.472	0.41	<0.01	1.34	<0.016	4.09
R16A	12.4	-	50	0.009	0.129	0.133	0.442	1.27	0.20	<0.07	4.25	<0.016	108.8
R16B	12.4	-	50	0.009	0.111	0.138	0.418	1.18	0.24	<0.07	3.77	<0.016	97.9

Table 9

1 Week Leach with Acetic Acid
ICP Leachate Analysis (ppm)

Sample	pH	Acid Addition (ml)	Amount of I.W. (g)	Mn	Mg	Al	Cu	Cr	Fe	Ni	Zn	Cd	Pb
R25A	5.6	50	0	4.50	38.9	1.12	0.14	0.056	48.2	0.152	1.03	<0.016	0.55
R25B	5.7	45	0	4.67	46.8	0.93	0.22	0.056	48.4	0.132	3.82	<0.016	0.30
R26A	5.5	110	4	14.3	58.3	2.04	0.19	0.25	55.9	0.415	>155	0.644	6.93
R26B	5.5	110	4	13.6	58.9	2.22	0.24	0.33	55.0	0.239	>155	0.748	7.58
R27A	7.1	185	15	8.57	51.4	0.23	0.44	0.092	0.31	0.160	>155	1.615	9.09
R27B	7.2	185	15	6.84	49.9	0.17	0.44	0.027	0.11	0.130	>155	1.685	10.2
R28A	12.3	185	50	0.008	0.26	0.26	0.31	0.23	0.04	<0.07	3.92	<0.016	299.5
R28B	12.3	185	50	0.020	0.30	0.32	0.38	0.17	0.10	<0.07	3.80	<0.016	293.5

NAA Leachate Analysis (ppm)

Sample	pH	Acid Addition	Amount of I.W. (g)	Mn	Mg	Al	Cu	Cr	Fe	Ni	Zn	Cd	Pb
R25A	5.6	50	0	5.17	30.7	1.11	<	359	0.59	108	0.060	110	59
R25B	5.7	45	0	4.63	34.4	0.270	366	0.49	113	0.071	120	120	66
R26A	5.5	110	4	14.3	45.0	1.70	<	696	2.69	170	0.069	129	102
R26B	5.5	110	4	13.8	45.0	1.88	<	725	2.81	164	0.088	135	74
R27A	7.1	185	15	8.62	37.0	0.143	<	1491	8.29	281	<	147	126
R27B	7.2	185	15	6.80	37.0	<	<	1560	8.16	279	<	143	111
R28A	12.3	185	50	<	<	<	<	2166	25.6	705	<	254	234
R28B	12.3	185	50	<	<	<	<	2338	25.6	746	<	272	255

Table 10

1 Month Leach with Acetic Acid
ICP Leachate Analysis (ppm)

Sample	pH	Acid Addition (ml)	Amount of I.W. (g)	Mn	Mg	Al	Cu	Cr	Fe	Ni	Zn	Cd	Pb
R41A	5.6	65	0	4.87	29.1	0.26	0.063	0.026	51.9	0.086	0.150	<0.016	<0.23
R41B	5.6	65	0	4.71	34.1	0.31	0.066	0.029	63.3	0.092	0.202	<0.016	<0.23
R42A	5.1	165	4	14.5	45.1	2.37	0.281	0.147	58.1	0.229	>155	0.505	9.79
R42B	5.1	165	4	14.3	55.8	1.65	0.515	0.113	50.1	0.245	>155	0.565	8.73
R43A	7.3	200	15	9.53	61.0	0.20	0.365	0.019	1.34	0.149	143.4	1.421	5.67
R43B	7.4	200	15	10.1	56.3	0.18	0.277	0.014	0.07	0.150	121.7	1.282	2.28
R44A	12.4	200	50	<0.001	0.21	0.28	0.316	0.199	0.036	<0.069	2.55	<0.016	201.8
R44B	12.4	200	50	<0.003	0.22	0.32	0.346	0.185	0.028	<0.069	2.53	<0.016	192.5

NAA Leachate Analysis (ppm)

R41A
R41B
R42A
R42B
R43A
R43B
R44A
R44B

Table 11

1 Week Leach Test Using Deionized Water
ICP Leachate Analysis (ppm)

Sample	pH	Acid Addition (ml)	Amount of I.W. (g)	Mn	Mg	Al	Cu	Cr	Fe	Ni	Zn	Cd	Pb
R17A	7.0	–	0	2.12	26.3	0.36	0.12	0.020	8.95	<0.07	0.235	<0.016	0.24
R17B	6.9	–	0	2.21	26.6	1.04	0.04	0.036	13.3	<0.07	0.421	<0.016	0.28
R18A	10.0	–	4	0.044	0.60	12.9	0.67	0.055	0.33	<0.07	0.204	0.035	0.37
R18B	10.3	–	4	0.108	1.36	7.95	0.71	0.074	0.69	<0.07	1.11	0.071	0.71
R19A	12.3	–	15	0.107	0.07	0.35	1.32	<0.01	0.31	<0.07	1.25	<0.016	0.80
R19B	12.4	–	15	0.107	0.08	0.91	1.52	0.020	0.20	<0.07	1.23	<0.016	0.85
R20A	12.5	–	50	<0.003	0.13	0.14	0.11	0.11	0.03	<0.07	2.77	<0.016	222.2
R20B	s12.5	–	50	<0.003	0.12	0.12	0.09	0.11	0.02	<0.07	2.76	<0.016	209.3

NAA Leachate Analysis (ppm)

Sample	pH	Acid Addition	Amount of I.W. (g)	Mn	Mg	Al	Cu	Cr	Fe	Ni	Zn	Cd	Pb
R17A	7.0	–	0	2.10	18.8	0.436	<	191	0.259	81.7	3.4	86.5	60
R17B	6.9	–	0	2.14	22.6	0.936	<	117	0.314	98.0	5.7	97.0	55
R18A	10.0	–	4	<	<	10.71	0.43	193	2.48	140	3.5	47.0	77
R18B	10.3	–	4	0.13	<	7.10	0.55	195	2.60	134	5.5	93.0	86
R19A	12.3	–	15	0.138	<	0.290	0.96	687	8.14	301	<	147	120
R19B	12.4	–	15	0.113	<	0.649	1.24	643	8.20	292	<	140	132
R20A	12.5	–	50	<	<	<	<	846	27.0	733	<	264	208
R20B	s12.5	–	50	<	<	<	<	810	25.9	710	<	261	250

Table 12

1 Month Leach with Deionized Water
ICP Leachate Analysis (ppm)

Sample	pH	Acid Addition (ml)	Amount of I.W. (g)	Mn	Mg	Al	Cu	Cr	Fe	Ni	Zn	Cd	Pb
R33A	6.9	-	0	2.93	28.9	0.16	0.10	0.02	10.0	<0.07	0.351	<0.016	<0.23
R33B	7.1	-	0	1.76	27.7	0.10	0.19	0.02	11.6	<0.07	0.156	<0.016	<0.23
R34A	8.0	-	4	3.33	19.9	0.09	0.27	0.02	0.75	0.08	9.78	0.023	0.47
R34B	7.6	-	4	1.52	10.9	0.42	0.65	0.02	0.74	<0.07	4.33	0.032	0.96
R35A	12.2	-	15	0.23	0.078	1.13	1.62	0.07	0.28	<0.07	2.07	<0.016	1.48
R35B	12.2	-	15	0.23	0.134	0.35	2.18	0.10	0.59	<0.07	2.39	<0.016	1.55
R36A	12.5	-	50	0.004	0.08	0.13	0.15	0.15	0.04	<0.07	2.65	<0.016	206.5
R36B	12.5	-	50	<0.003	0.08	0.13	0.17	0.16	0.02	<0.07	2.60	<0.016	183.3

NAA Leachate Analysis (ppm)

Sample	pH	Acid Addition	Amount of I.W. (g)	Mn	Mg	Al	Cu	Cr	Fe	Ni	Zn	Cd	Pb
R33A													
R33B													
R34A													
R34B													
R35A													
R35B													
R36A													
R36B													

Table 13

1 Week Leach Test with Municipal Leachate
ICP Leachate Analysis (ppm)

Sample	pH	Acid Addition (ml)	Amount of I.W. (g)	Mn	Mg	Al	Cu	Cr	Fe	Ni	Zn	Cd	Pb
R29A	6.9	-	0	2.10	68.5	0.60	0.14	0.05	4.76	0.073	0.096	<0.016	<0.23
R29B	6.8	-	0	2.33	68.8	0.49	0.27	0.05	8.38	0.084	0.285	<0.016	<0.23
R30A	7.8	-	4	1.20	44.2	0.14	0.21	0.06	4.01	0.095	4.07	<0.016	0.47
R30B	7.8	-	4	1.11	46.7	0.30	0.23	0.08	5.57	0.111	5.57	<0.016	0.96
R31A	12.2	-	15	0.047	0.10	0.67	0.72	<0.012	0.55	0.100	0.93	<0.016	1.48
R31B	12.1	-	15	0.042	0.12	19.1?	0.73	0.013	0.42	0.082	0.45	<0.016	1.55
R32A	12.6	-	50	0.009	0.09	0.12	0.62	0.18	0.02	<0.07	3.68	<0.016	206.6
R32B	12.6	-	50	0.013	0.10	0.12	0.59	0.11	0.08	<0.07	3.49	<0.016	183.3

NAA Leachate Analysis (ppm)

Sample	pH	Acid Addition	Amount of I.W. (g)	Mn	Mg	Al	Cu	Cr	Fe	Ni	Zn	Cd	Pb
R29A													
R29B													
R30A													
R30B													
R31A													
R31B													
R32A													
R32B													

Table 14

1 Month Leach Test with Municipal Leachate
ICP Leachate Analysis (ppm)

Sample	pH	Acid Addition (ml)	Amount of I.W. (g)	Mn	Mg	Al	Cu	Cr	Fe	Ni	Zn	Cd	Pb
R45A	7.16	-	0	3.98	68.2	0.15	0.25	0.021	4.13	<0.07	0.39	<0.016	<0.23
R45B	7.82	-	0	3.24	67.4	0.34	0.21	0.023	7.50	<0.07	0.30	<0.016	<0.23
R46A	7.52	-	4	3.98	68.9	0.09	0.21	0.032	2.98	0.08	4.70	<0.016	0.48
R46B	7.51	-	4	3.74	60.5	0.09	0.22	0.024	3.20	0.08	6.97	<0.016	0.70
R47A	7.91	-	15	0.087	1.12	4.33	0.28	0.014	0.15	<0.07	0.14	<0.016	<0.23
R47B	7.80	-	15	1.21	12.6	0.19	0.17	<0.012	01.61	<0.07	3.81	<0.016	0.43
R48A	12.56	-	50	0.017	0.074	0.08	2.46	0.32	0.03	<0.07	1.87	<0.016	70.67
R48B	12.56	-	50	0.048	0.113	0.12	2.33	0.28	0.23	<0.07	1.99	<0.016	65.26

NAA Leachate Analysis (ppm)

Sample	pH	Acid Addition	Amount of I.W. (g)	Mn	Mg	Al	Cu	Cr	Fe	Ni	Zn	Cd	Pb
R45A													
R45B													
R46A													
R46B													
R47A													
R47B													
R48A													
R48B													

EFFECTS OF INCREASING AMOUNTS OF NON-POLAR ORGANIC LIQUIDS IN DOMESTIC WASTE LEACHATE ON THE HYDRAULIC CONDUCTIVITY OF CLAY LINERS IN SOUTHERN ONTARIO

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Key words: Non-polar Organics, Organics, Domestic Waste, Leachate, Hydraulic Conductivity, Clay Liners.

ABSTRACT

The hydraulic conductivity, k, of Sarnia soils, mixed with pure liquids varies from 5 x 10^{-9} to 1 x 10^{-4} cm/s as the dielectric constant varies form 80 to 2. Permeation of liquids of low dielectric constant (benzene, cyclohexane, xylene) through compacted, water-wet samples ($k \approx 10^{-8}$ cm/s at e = 1.0) showed no changes in k, the hydrophobic liquids displacing only 10% of the pore water from microchannels in the clays. Sequential permeation, first by alcohol (ε = 30) followed by a non-polar aromatic yields 10-fold, then 1000-fold, increases in k. The alcohol apparently acts as a mutually soluble association liquid enabling the aromatics to contract the clay double layers.

Current testing of Southern Ontario clays with domestic waste leachates shows little effect on k despite significant retardation and fixation of potassium. Sterilization and bacterial culturing requirements will be discussed.

Results from preliminary testing of clays using domestic waste leachate spiked with known amounts of simple aromatics, with and without alcohol as an association liquid, will be presented, in a first attempt to define threshold concentrations required to initiate detrimental increases in the hydraulic conductivity of clay barriers.

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ABSTRACT

The hydraulic conductivity, **k**, of Sarnia soils, mixed with pure liquids varies from 5 x 10^{-9} to 1 x 10^{-4} cm/s as the dielectric constant varies from 80 to 2. Permeation of liquids of low dielectric constant (benzene, cyclohexane, xylene), through compacted, water-wet samples ($k \approx 10^{-8}$ cm/s at $e = 1.0$) showed no changes in **k**, the hydrophobic liquids displacing only 10% of the pore water from microchannels in the clays. Sequential permeation first by alcohol ($\varepsilon = 30$) followed by a non-polar aromatic yields 10-fold, then 1000-fold increases in **k**, the alcohol apparently acting as a mutually soluble association liquid enabling the aromatics to contract the clay double layers.

Currently testing of southern Ontario clays with domestic waste leachates shows little effect on **k** despite significant retardation and fixation of potassium. Sterilization and bacterial culturing requirements will be discussed.

Preliminary testing of clays using domestic waste leachate spiked with known amounts of simple aromatics with and without alcohol as an association liquid will be presented in a first attempt to define threshold concentrations required to initiate detrimental increases in the hydraulic conductivity of clay barriers.

INTRODUCTION

Recent research has disclosed that non-polar organic liquids (low dielectric constant) have the capacity to increase the hydraulic conductivity of clay barriers by several orders of magnitude. On the other hand, recent work has also shown that typical domestic waste leachate normally has little effect on the hydraulic conductivity and may actually cause it to decrease. Since co-disposal (simultaneous or alternate disposal of toxic and non-toxic waste) has been practised in the past, it is important to know at what concentration levels organic liquids create a threat to the integrity of clay barriers (natural or compacted) below domestic waste sites. Since cleaning solvents, paint residues, alcohols, pesticides, etc., are regularly discarded with household garbage, even normal domestic waste may create leachate with significant contents of dissolved organic species.

The purpose of this project is to establish the threshold levels at which simple benzene-type compounds present in raw domestic waste leachate will damage a clay barrier by increasing its hydraulic conductivity. Since these low dielectric constant liquids are almost insoluble in water, alcohols will be used as "association" liquids to increase the dissolved amounts thus permitting ingress into the clay barrier.

Since this project only commenced in September 1985, this paper presents a brief summary of previous background work already completed and our proposed testing program. Clay/organic liquid compatibility is briefly reviewed followed by new work on clay/domestic waste compatibility. This is followed by an assessment of the experimental problems to be overcome in the study of spiked leachates and their influence on clay barriers.

CLAY/ORGANIC LIQUID COMPATIBILITY

Pure Liquid Systems

The dramatic effect of organic liquids on clayey soils was recently discussed at some length by Fernandez and Quigley, 1985. Figure 1 illustrates the enormous range in hydraulic conductivity obtained using several pure liquids moulded with dry brown silty clay from Sarnia, Ontario (k $\approx 10^{-9} - 10^{-4}$ cm/s). At a given void ratio polar water ($\varepsilon = 80$) produced the lowest k values, alcohol and acetone ($\varepsilon = 20$-35) intermediate k values, and aromatic compounds ($\varepsilon \approx 2$) the highest **k** values. This spread of values was obtained by direct measurement of **k** using constant flow rate hydraulic conductivity equipment and was very similar to earlier values obtained by consolidation testing (Mesri and Olson, 1971).

The significance of the correlation between k and ε is further illustrated on Figure 2 for a constant void ratio of unity. It should be noted that each soil was moulded dry with the pure liquid in question. Under these conditions, each liquid yields complete control on the clay/double layer system that controls **k**. For example, polar water effectively hydrates both the clay surface and the adsorbed cations, producing a thick double layer that "clogs" the soil preventing easy flow and reducing **k**. The low dielectric fluids are non-polar, do not hydrate the cations other than by geometric packing resulting in a very thin double layer. At a given void ratio, more of the pore space is filled with "free" liquid resulting in very high **k** values.

As discussed by Fernandez and Quigley, 1985, the above phenomena can also be described in terms of the Gouy-Chapman Theory of potential (Figure 3).

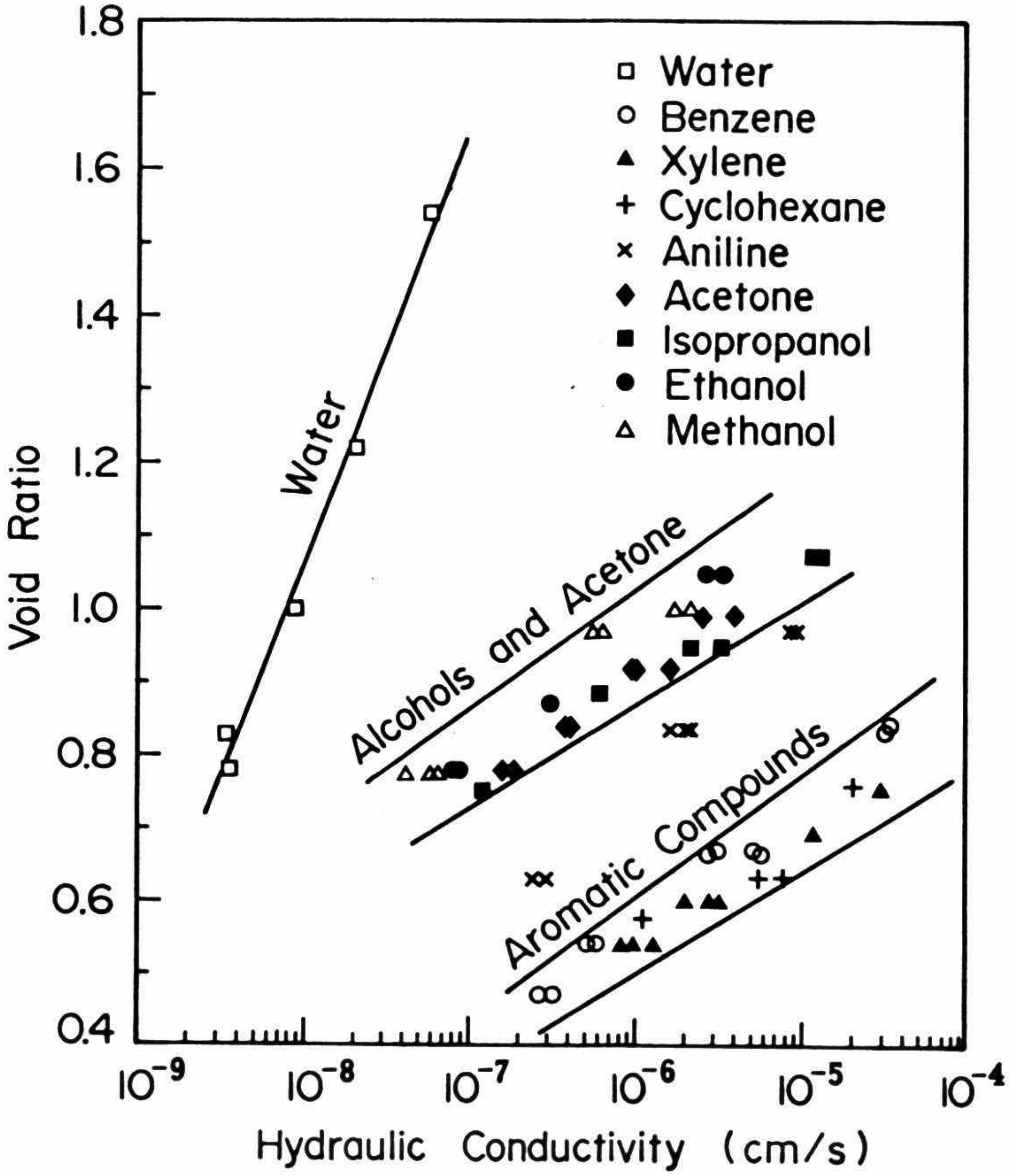

FIGURE 1. HYDRAULIC CONDUCTIVITY VS VOID RATIO. ALL SAMPLES MOULDED AND PERMEATED WITH LIQUID INDICATED (Directly from Fernandez and Quigley, 1985).

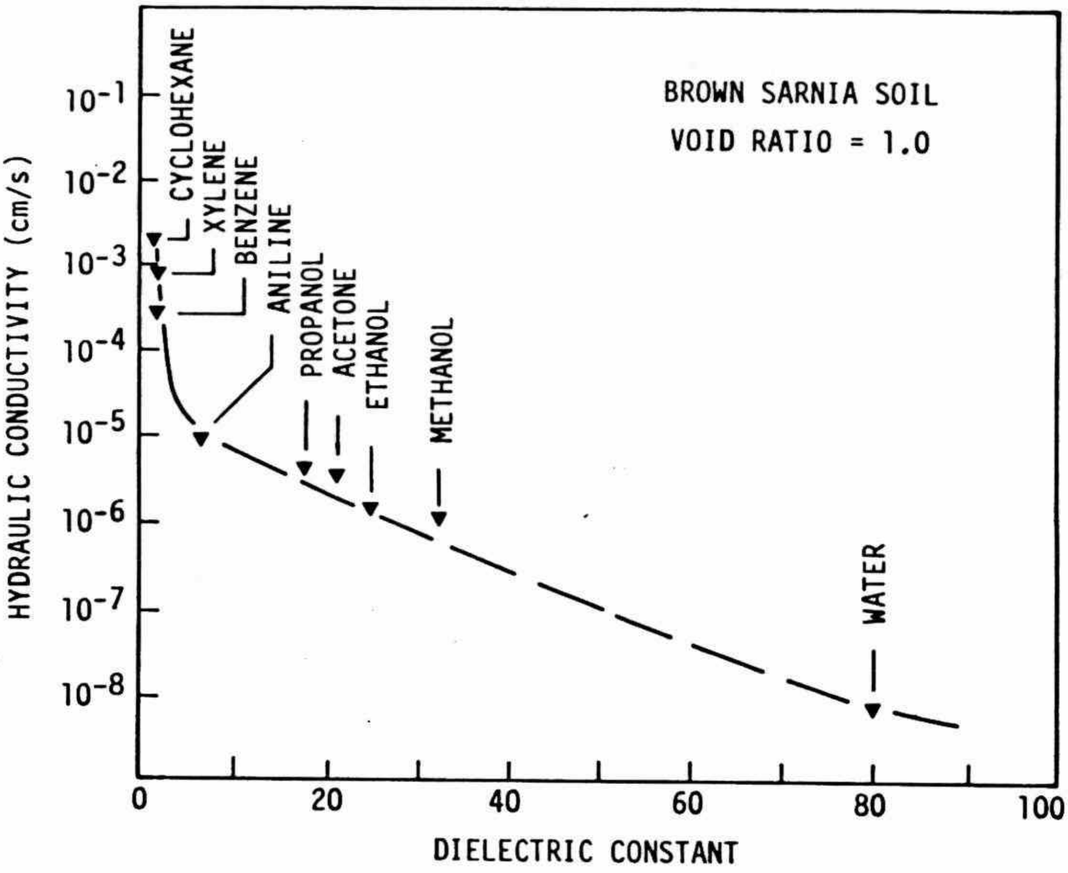

FIGURE 2. HYDRAULIC CONDUCTIVITY VS DIELECTRIC CONSTANT. DATA FROM FIGURE 1. (Adapted from Fernandez and Quigley, 1985).

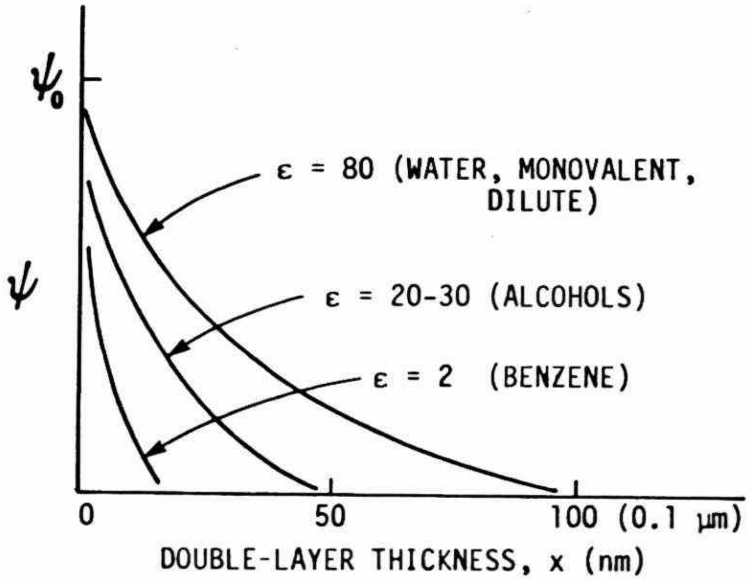

FIGURE 3. DOUBLE LAYER THICKNESS RELATED TO DIELECTRIC CONSTANT OF PORE FLUID (Directly from Fernandez and Quigley, 1985).

Sequential Permeation

Invariably, clay barriers exist with water in the pore spaces and subsequent permeation with a liquid hydrocarbon should not be expected to behave like the pure systems just described.

As shown on Figure 4, brown Sarnia soil compacted with water at a void ratio = 0.98 was first permeated with water for about 1 pore volume (1 P.V.) yielding a reference **k** = 10^{-8} cm/s and a nearly saturated soil. It was then permeated with benzene for another 2 P.V. After only 0.6 P.V. the effluent from the specimens consisted of pure benzene and the hydraulic conductivity remained constant. The arrival of 50% benzene in the effluent at only 0.28 P.V. strongly suggests permeation through channels or micropores. When the sample was dismantled, this was confirmed by the presence of only 8% benzene in the pore spaces of the soil. The combination of a very high gradient ($i = 500$) and the hydrophobicity of the benzene to water would explain this behaviour.

These results are quite different from other work which showed rapid increases in **k** with permeation by low dielectric liquids. (Anderson and Brown, 1981; Anderson et al, 1982; Brown et al, 1983). A major problem appears to be compaction induced cracking which enables early arrival of hydrophobic permeants.

The same sequence of events using alcohol as the second permeant is shown on Figure 5. In this case k increased gradually from 10^{-8} cm/s to 10^{-7} cm/s after the passage of 2 P.V. of methanol and the effluent concentration never did quite reach influent values. The arrival of 50% concentration after 0.75 P.V. indicates more even flow through the sample. When dismantled this sample contained 94% methanol in the pore spaces and only 6% water.

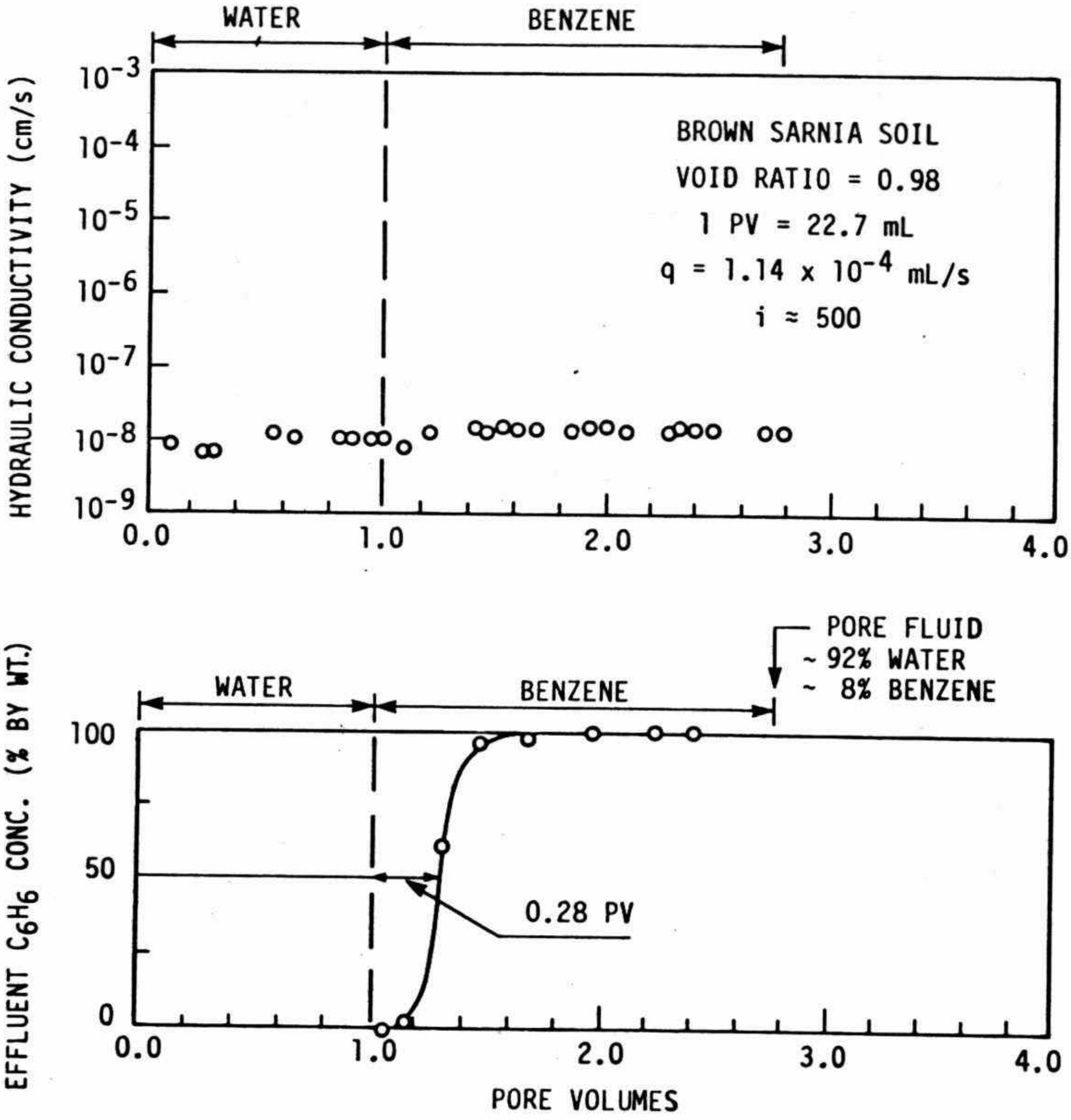

FIGURE 4. PERMEATION OF BENZENE THROUGH WATER SATURATED CLAYEY SOIL. HYDRAULIC CONDUCTIVITY AND EFFLUENT CONCENTRATION VS PORE VOLUMES PASSED THROUGH (Directly from Fernandez and Quigley, 1985).

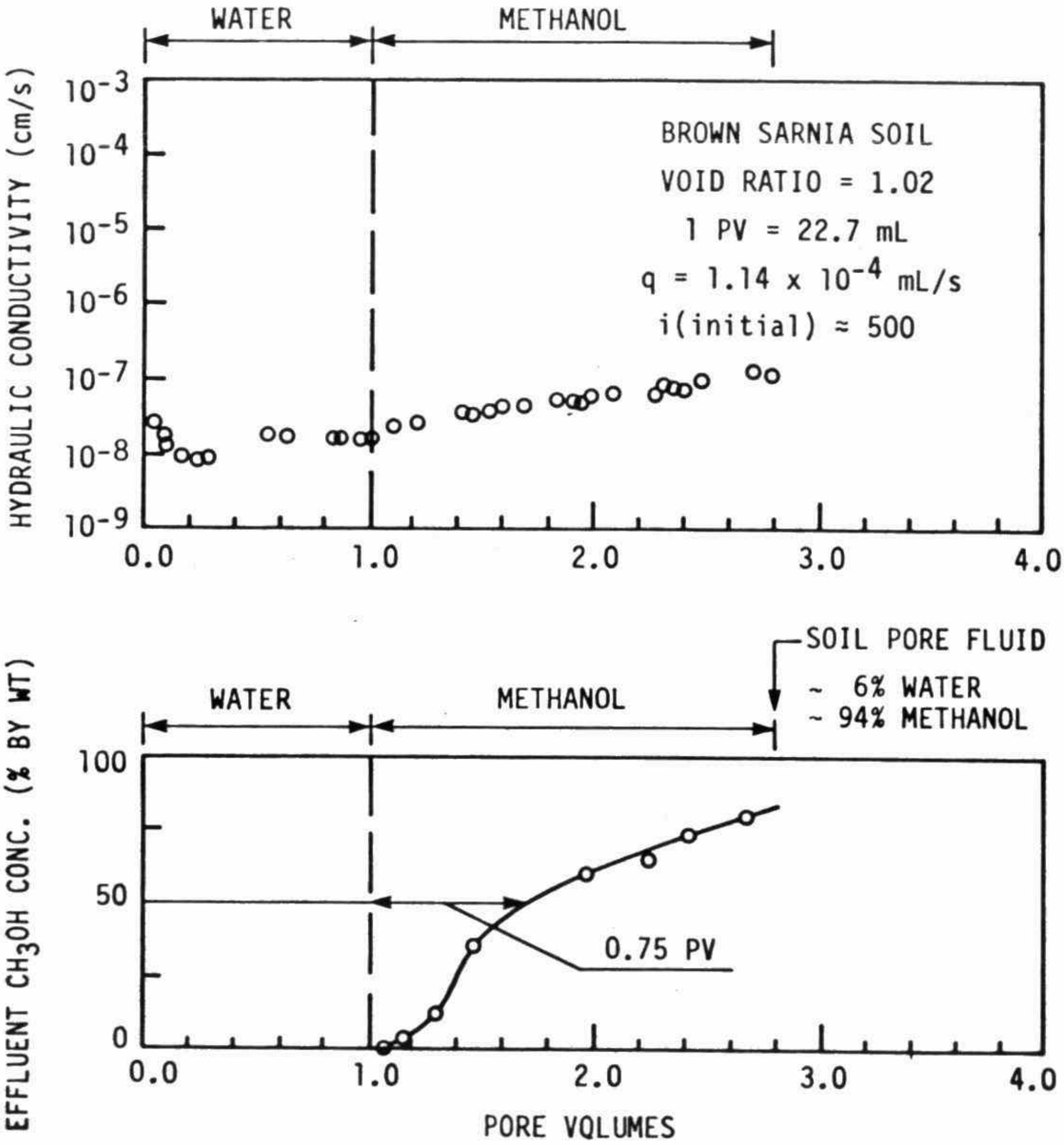

FIGURE 5. PERMEATION OF METHANOL THROUGH WATER SATURATED CLAYEY SOIL, HYDRAULIC CONDUCTIVITY AND EFFLUENT CONCENTRATION VS PORE VOLUMES (Directly from Fernandez and Quigley, 1985).

The solubility of alcohol in water enables it to diffuse into the double layer position and contract the double layer as illustrated on Figure 6. The contraction (flocculation) creates free pore space causing the 10-fold rise in **k**.

The results of three-stage sequential permeation by water, ethanol and benzene are illustrated on Figure 6. The water-ethanol sequence yielded results similar to those described for methanol, with ethanol occupying 65% of the pore space at the end of 3 P.V. of ethanol permeation. Subsequent permeation by benzene now caused a dramatic increase in **k** to values of close to 10^{-4} cm/s. This increase is attributed to the presence of alcohol which "solubilizes" the hydrophobic benzene, enabling it to enter and contract the clay double layer, resulting in the dramatic increase in **k**. At the end of testing, benzene occupied only ≈ 30% of the pore space.

The object of this research program is to permeate domestic waste leachate, spiked with organics solubilized by alcohol as an association liquid, through typical clay barrier soils from southern Ontario.

CLAY/DOMESTIC LEACHATE COMPATIBILITY

Samples of compacted Sarnia clay from 0.3 m depth and 11 m depth were permeated with London landfill leachate as shown on Figures 7, 8 and 9. Resultant **k** values at the end of testing were as follows:

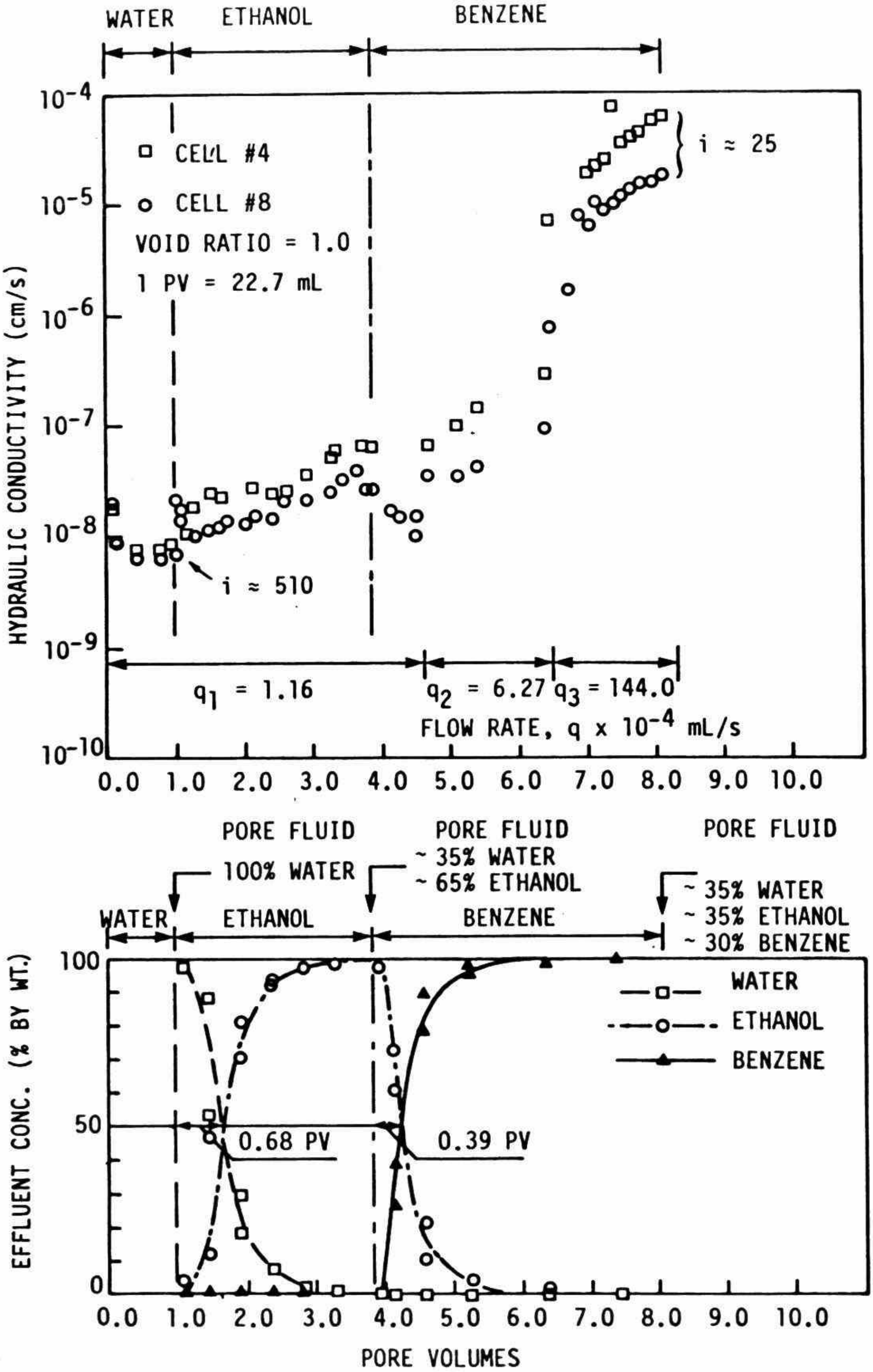

FIGURE 6. SEQUENTIAL PERMEATION: WATER, ETHANOL, BENZENE.

Soil	k_f
Brown, e = 0.74, 0.3 m	1.5×10^{-9} cm/s
Brown, e = 0.54, 0.3 m	1.0×10^{-9} cm/s
Grey, e = 0.54, 11 m	4.0×10^{-9} cm/s

The near surface soils contain significant amounts of smectite (up to 15%) compared to the grey clays (~ 2%) resulting in lower **k** values at a given void ratio, although interpretation is made very complex by compaction induced cracking of the samples. The test illustrated by Figure 8 is a problem test which will have to be repeated because of the erratic response of **k** versus pore volumes curve when the permeant was changed from water to leachate.

High quality test results for a brown clayey soil compacted to a relatively high void ratio of 0.74 are shown on Figure 7. The results show that K^+ is strongly retarded by these weathered smectite soils suggesting the possibility of potassium fixation opening of free pore space as a result of double layer contraction and interlayer collapse. This is not reflected in the curve of **k** vs pore volumes which shows a final **k** value of ~ 1.5×10^{-9} m/s, slightly below the initial value for water. This observation is consistent with those of Griffen et al, (1976), Daniel and Liljestrand (1984), Quigley et al (1985) who generally observe little or no damaging effects of domestic leachate migration through clay barriers.

Other important features of the C/C_o vs P.V. plot are:

a) Calcium and magnesium are displaced by cations in the leachate arriving "early" and producing a concentration pulse in the effluent equivalent to a hardness halo,

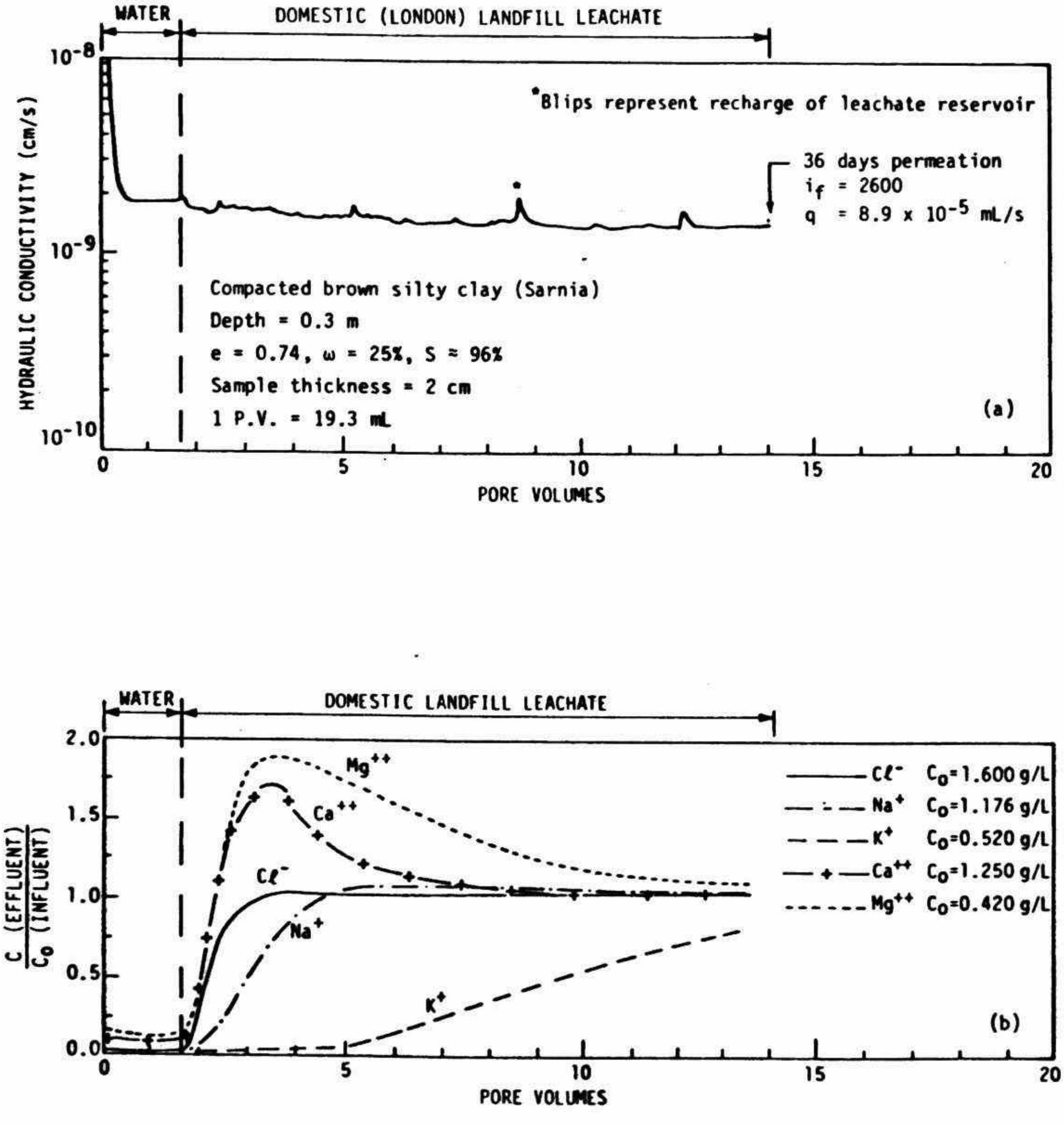

FIGURE 7. SOIL/DOMESTIC LEACHATE COMPATIBILITY: (a) HYDRAULIC CONDUCTIVITY, (b) EFFLUENT CHEMISTRY VS PORE VOLUMES OF LEACHATE; WEATHERED SARNIA SOIL, 0.3 m DEPTH, COMPACTED, VOID RATIO = 0.74.

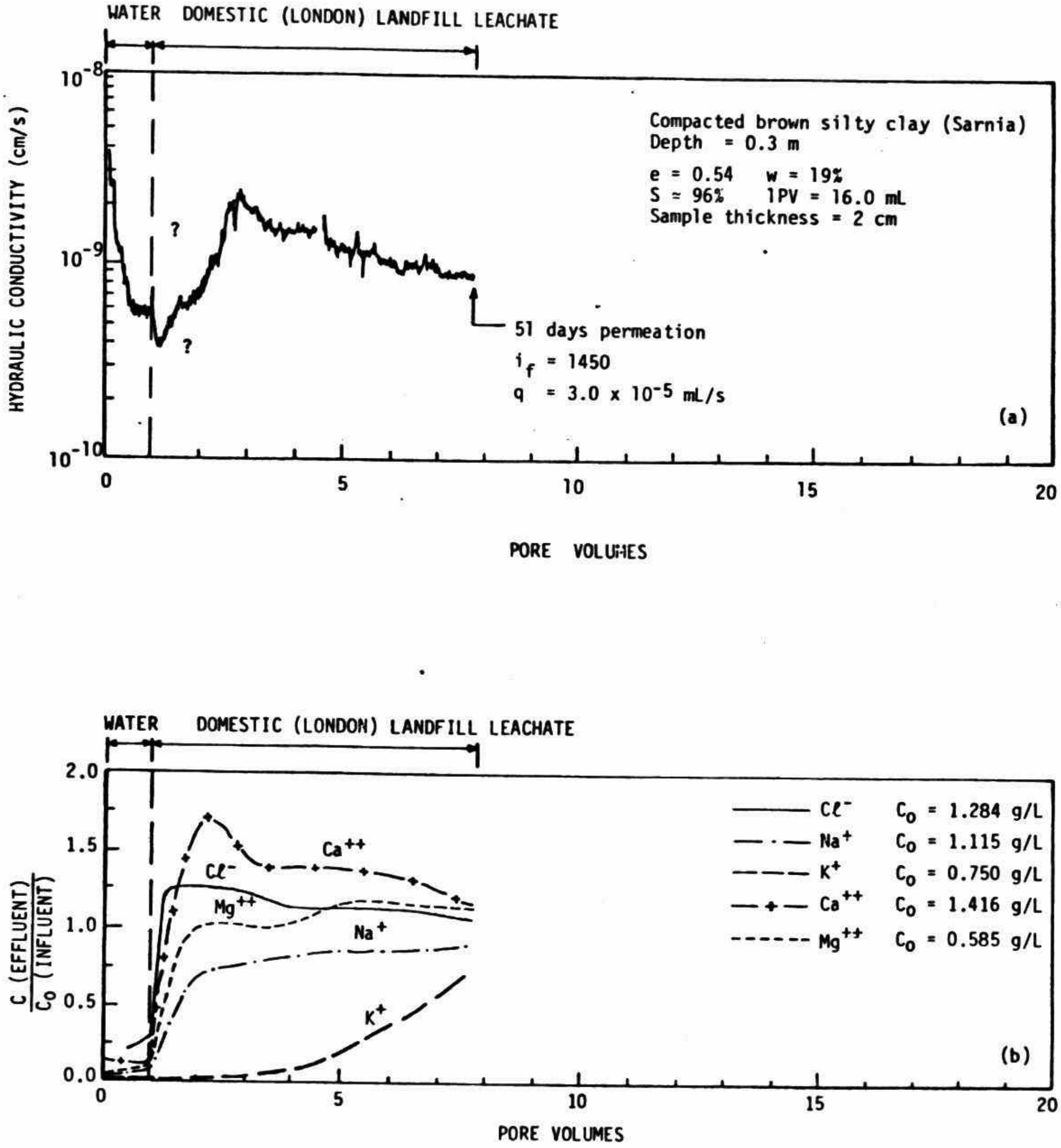

FIGURE 8. SOIL/DOMESTIC LEACHATE COMPATIBILITY: (a) HYDRAULIC CONDUCTIVITY, (b) EFFLUENT CHEMISTRY VS PORE VOLUMES OF LEACHATE; WEATHERED SARNIA SOIL, 0.3 m DEPTH, COMPACTED, VOID RATIO = 0.54.

b) Sodium is slightly retarded (C/C_o = 0.5 at 1.4 P.V.) apparently indicating adsorption and replacement of Ca^{++} and Mg^{++}

c) Chloride appears unattenuated and arrives early, C/C_o reaching 0.5 at only 0.6 P.V.

d) The chloride curve suggests that this particular sample, compacted wet of optimum, is relatively free of fractures but still contains macropore channels that cause early arrival of the conservative chloride species.

Similar curves (Figure 8) are presented for the same brown Sarnia soil compacted to a lower void ratio of 0.54. In this particular case, the high mass of soil (lower void ratio) should result in greater K^+ retardation, rather than the lesser retardation indicated (compared on Figure 7). Also, the chloride arrives very early (C/C_o = 0.5 at less than 0.1 P.V.) indicating preferential flow paths probably directly related to compaction induced fracturing of this much harder, lower void ratio specimen.

Finally, similar curves are presented on Figure 9 for grey Sarnia soil from 11 m depth, compacted to e = 0.54. All listed inorganic species arrive very early (C/C_o = 0.5 at 0.1 to 0.5 P.V.) indicating that macropores and compaction induced fractures dominate the flow regime in spite of the relatively low gradient used (i_f = 150). Also these grey clays contain very little collapsible smectite (1-2%) so the K^+ would be much less retarded for this reason also.

A preliminary summary plot showing the effects of soil weathering and void ratio on K^+ retardation is shown on Figure 10. Since oxidation weathering of chloride increases the smectite content towards the surface, the samples should show increasing K^+

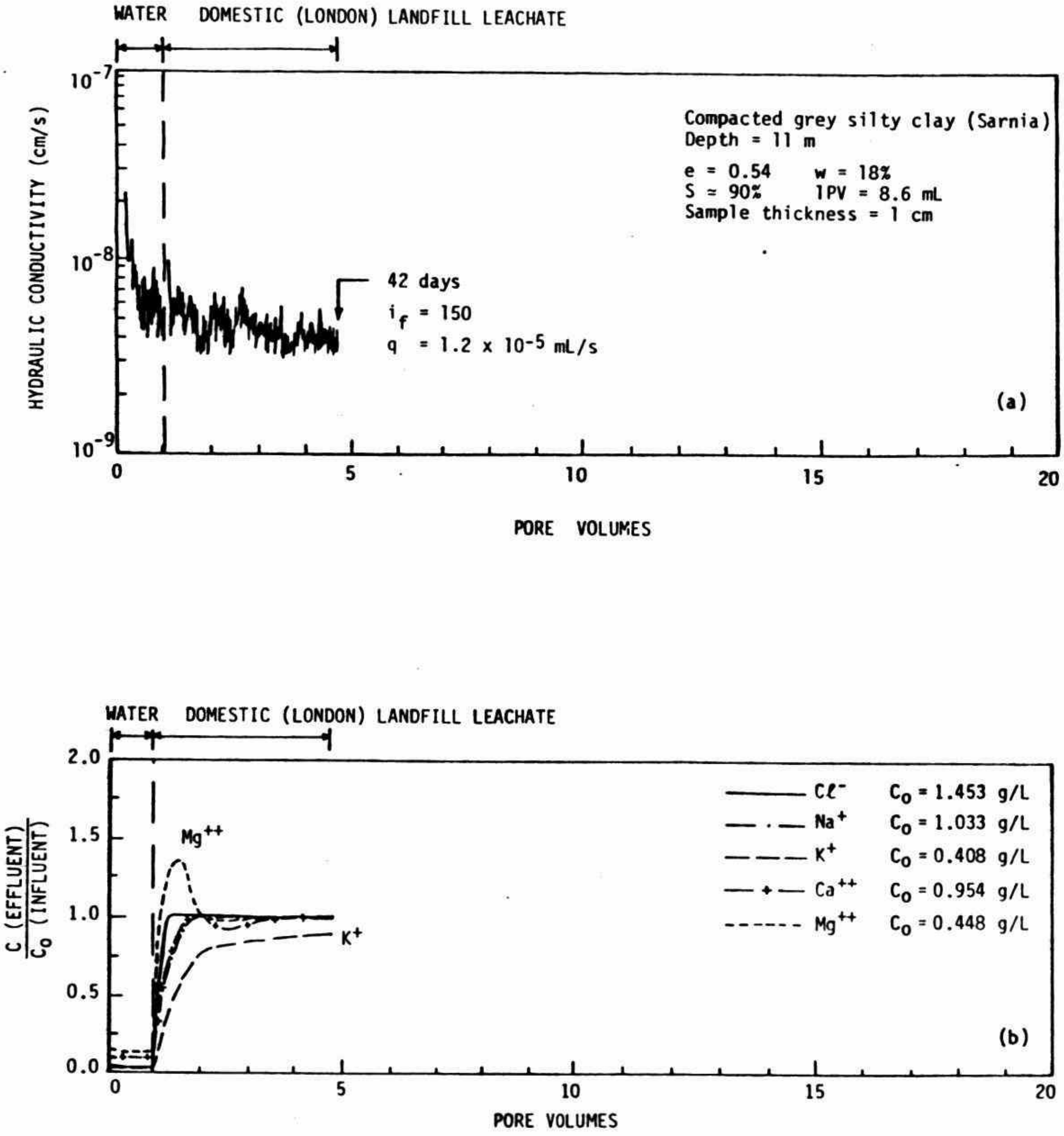

FIGURE 9. SOIL/DOMESTIC LEACHATE COMPATIBILITY: (a) HYDRAULIC CONDUCTIVITY, (b) EFFLUENT CHEMISTRY VS PORE VOLUMES OF LEACHATE; UNWEATHERED SARNIA SOIL, 11 m DEPTH, COMPACTED, VOID RATIO = 0.54.

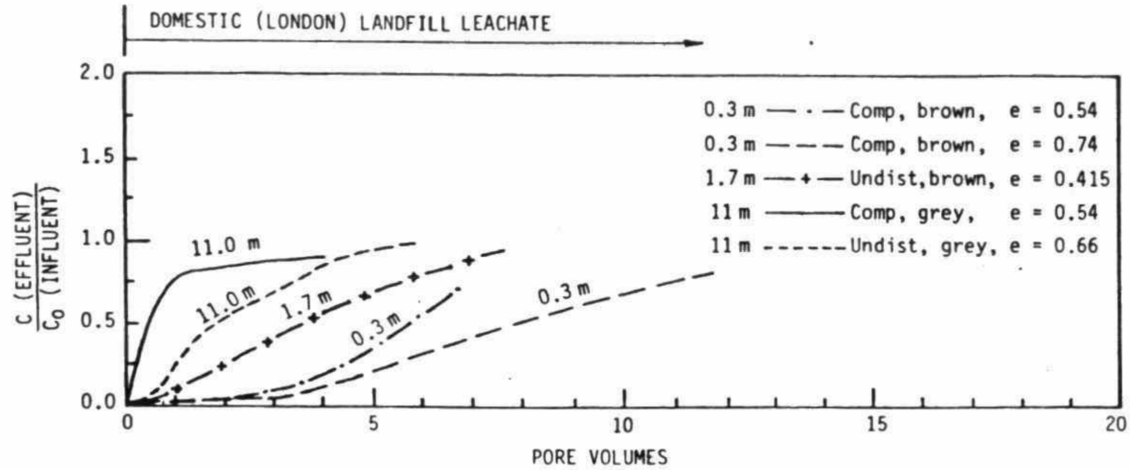

FIGURE 10. POTASSIUM RETARDATION ILLUSTRATED BY EFFLUENT CONCENTRATIONS FOR SARNIA CLAYEY SOILS FROM THREE DEPTHS.

retardation towards the surface and this is clearly shown by the curves for 0.3, 1.7 and 11.0 m depths. This particular trend (mineralogy-depth control on K^+ retardation) dominates in spite of having different void ratios and both compacted and undisturbed samples on the plot.

The lesser retardation by the compacted brown clay at $e = 0.54$ compared to the one at $e = 0.74$ has already been attributed to compaction induced fracturing. Finally, the lesser K^+ retardation by the grey compacted clay at $e = 0.54$ compared to the undisturbed grey clay at $e = 0.66$ is also attributed to compaction induced fractures. In summary, it may be concluded that artifacts of compaction (peds, interped macropores, shear fractures, etc.) are a very serious factor in interpreting hydraulic conductivity tests results.

TESTING PLANS AND PROBLEMS

Testing plans call for two major series of permeation studies using water and domestic leachate as the stock permeants. To these stocks, variable percentages of alcohol and simple aromatics such as benzene will be added in increments to establish the threshold levels at which major increases in **k** might develop.

Major problems foreseen are listed as follows:

1. Selection of test soils:
   Most of the brown weathered soils of southern Ontario contain smectite as a result of oxidation of original soil chlorites present in underlying grey soils. The brown soils are preferred since they are less pervious than the grey soils because of their smectite content. However, they are also

more susceptible to shrinkage by K^+ fixation and adsorption of organics. Because of these reactivity problems, grey soils are probably preferable to brown soils in general.

2. Cracking may be a very serious problem with some vermiculitic soils since K^+ fixation causes interlayer collapse from 1.4 nm to 1.0 nm and also causes a sharp, permanent drop in the cation exchange capacity. Lower charge montmorillonites collapse to some extent but the C.E.C. is not reduced.
3. Microbial problems may be severe during long term tests at low hydraulic gradients. Problems would include degradation of trace amounts of organics and pore clogging by bacterial colonies. High gradient tests may be less affected by clogging.
4. Sterilization of both the soils and permeants by 2.5 Mrads of cobalt γ-radiation is presently being used but regrowth of apparently dormant systems after 8 weeks of permeation is an unexpected problem. Both sterilized and non-sterilized systems should probably be tested.
5. Storage of stock permeants and spiked stock permeants for several months before or during use also produces stability problems for leachate as iron flocs percipitate, oxidation occurs and biological systems change.
6. High gradient tests will be used to accelerate testing programs to a time length of about 3 months. Low gradient tests more characteristic of field conditions take years to conduct, resulting in diffusion dominated migration superimposed by severe biological problems.

7. Compaction induced fractures around soil peds present a severe problem with respect to channelling of permeants especially at high gradients. Early breakthrough times mean that effluent concentrations reach influent values very soon during testing and reaction with the soil must take place by diffusion away from the flow channels. Hopefully such a situation is not characteristic of a well constructed liner.

ACKNOWLEDGEMENTS

The work on organic liquid interaction with clay soils was completed in 1984 using funds from the Natural Sciences and Engineering Research Council of Canada as was some of the early work on domestic waste leachate. Ontario Ministry of the Environment Funds have been used for domestic waste leachate studies on low void ratio soils more characteristic of actual clay barriers.

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GEOMECHANICAL INVESTIGATION OF NEAR-SURFACE FRACTURES IN CLAY TILLS

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Key words: Clay Till, Nanticoke, Southern Ontario, Waste Disposal, Disposal Sites, Leachate, Near-surface Fractures, Contaminant Migration.

ABSTRACT

The purpose of this investigation is to characterize the nature and variability of near-surface fractures in clay tills of Southern Ontario. To accomplish this, four research sites have been chosen to provide a regional as well as geomorphological variation to the clay soils. These sites are located in the following: Haldimand clay plain at Nanticoke, Essex clay plain near Essex, Lambton clay plain near Sarnia and Port Stanley till near London.

The field work component of this research involves digging trenches with a backhoe down to depths of 13 feet to permit fracture mapping and block sampling, as well as auger drilling and Shelby tube sampling down to a maximum depth of 50 feet. The sampling tubes used have an inside diameter of 4.5 inches.

The laboratory component of this research involves various strength and deformability tests using a triaxial cell and mineralogical analysis using x-ray diffraction. The triaxial tests will determine shear strengths and stress-strain relationships of the clays in triaxial compression and extension. A hydraulic fracturing method will also help determine the tensile strength of the fractured clays in the triaxial cell.

Comparing fracture orientation data, mineralogical analysis results and geotechnical properties of the clay soils, a good indication of the regional variability and behaviour of near-surface fractures in Southern Ontario clays shall be provided.

The results of this investigation will be directly applicable in assessing the suitability of siting waste disposal facilities in surface clay deposits. The behaviour of near-surface fractures during construction and their possible role in future contaminant migration from waste impoundments shall be better understood.

GEOMECHANICAL INVESTIGATION OF NEAR-SURFACE FRACTURES IN CLAY TILLS

Part A: Fracture Mapping at Three Sites in Southwestern Ontario

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INTRODUCTION

The purpose of this research is to attempt to characterize, on a regional scale, the nature and behaviour of near-surface fractures in clays and clay tills of southwestern Ontario. It is well recognized that the geotechnical properties of fractured clays are greatly affected by the surface characteristics, orientation and spacing of the fractures. Mahar (1983), Marsland (1971) and Lo (1970) have pointed out the difficulty of obtaining a consistent measure of fractured clay strength because of the effect of sample size and the inherent anisotropy exhibited by this difficult material. However, the geomechanical behaviour of fractured clays is an important factor when determining slope stability, earth pressures and bearing capacity related to various types of engineering works. The purpose of the present research is to acquire a better understanding of the behaviour of fractured clays with respect to the construction of liquid waste impoundments and industrial and municipal landfills.

Because of their very low permeability and wide spread occurence, the Quaternary clays and clay tills of southwestern Ontario have become a prime media for the disposal of liquid and solid wastes. Work done by Desaulniers (1980) has confirmed that the hydraulic conductivities of these clay deposits range between 10-7 and 10-8 cm/s and that the fractures in the weathered zones of these deposits, although abundant, do not appear to substantially increase the bulk hydraulic conductivity as determined by field hydraulic conductivity tests. The oxidation weathering of chlorite to smectite has been observed in the upper 2 m. of Sarnia soils by Quigley and Ogunbadejo (1973) which may provide a mechanism by which fractures are sealed. Desaulniers concluded that groundwaters at depth are of Early Holocene or Late Pleistocene origin and that molecular diffusion is the dominant mechanism for migration of environmental isotopes (tritium and oxygen-18) and dissolved solids. Therefore, in their undisturbed state, the thick clayey deposits should provide long term containment of leachates.

The hypothesis put forward by the present research is that the construction of waste impoundments in clayey deposits could alter the existing stress regime to one that may reopen existing fractures or create new fractures around the excavation bottom subjected to even minor tensile stresses.

In this paper, we describe the procedures and results of detailed fracture mapping in the field. Sites were chosen to assure regional and morphological variation in the fracture data collected (Figure 1). This is essential to permit extrapolation

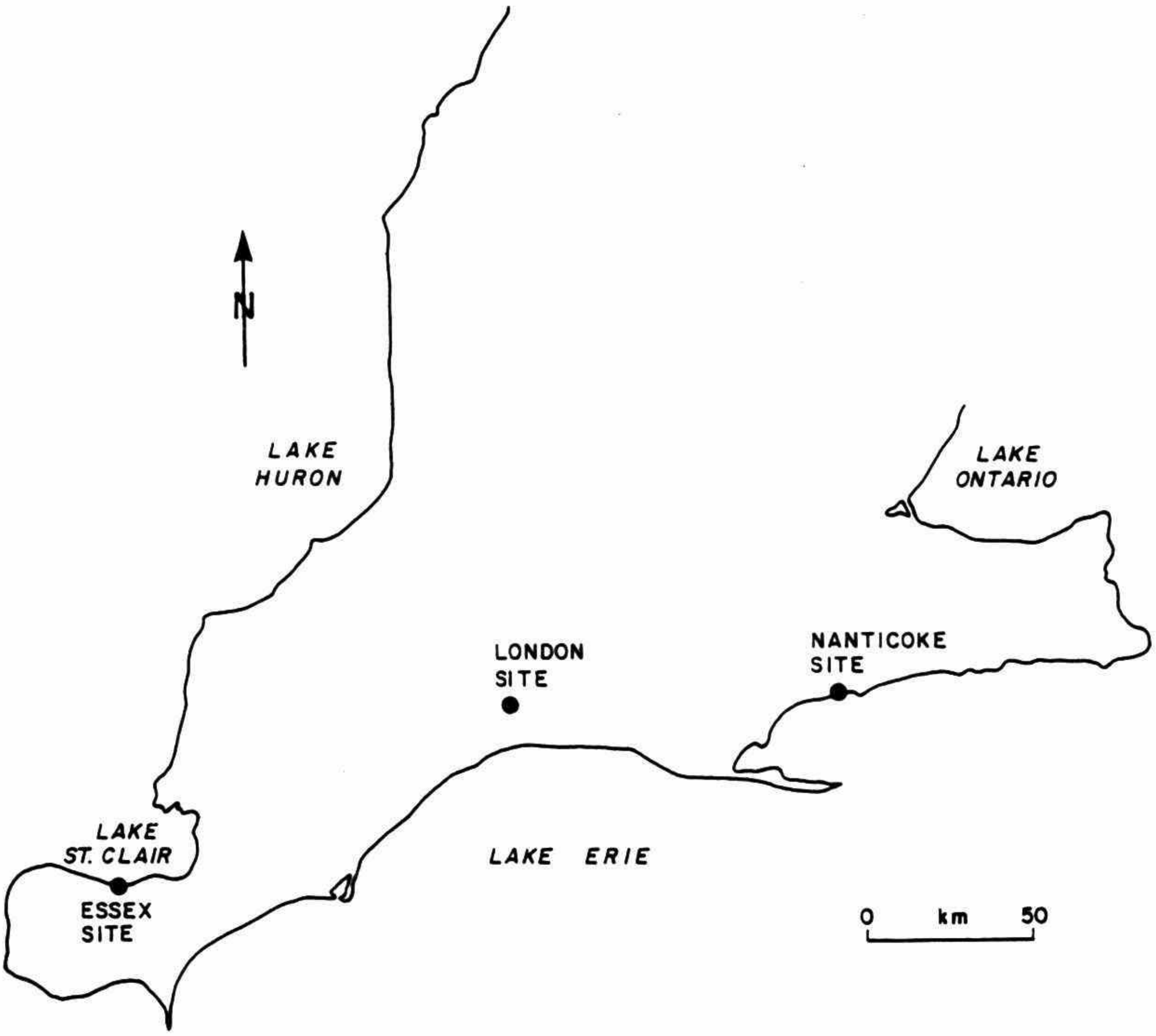


Figure 1

LOCATION MAP

of fractured clay behaviour into other regions of the province. It is also believed that a clearer understanding of the origin of these fractures will permit better evaluation of the role they may play in the migration of contaminants and in the general stability of earthworks.

The term "fracture" is used herein as a general term applied to weakness planes in soil and rock. Since the nature of the fractures in clays is uncertain, the use of the terms "fissure" and "joint" were deemed misleading. The term "fissure" is used by geologists to describe open large discontinuities, whereas engineers use the same term to describe small discontinuities. The term "joint" is used to describe small and large closed discontinuities by geologists, and open or closed large discontinuities by engineers (Fookes and Deness, 1969).

GEOLOGY OF RESEARCH SITES

Nanticoke Water Pumping Station

The Nanticoke Water Pumping Station forms part of the Central Haldimand-Norfolk Water System and is located on County Road 55 across from the Ontario Hydro Generating Station on the north shore of Lake Erie. This site is within the Haldimand clay plain as described by Chapman and Putnam (1966), consisting mostly of glaciolacustrine clays and tills deposited during advances and retreats of the Erie and Halton ice lobes. The thickness of the Quaternary deposits in the Simcoe area varies considerably from 40 m. to zero at bedrock outcrops of the Onondaga Escarpment (Barnett, 1978). The Nanticoke area itself consists of massive to laminated deepwater glaciolacustrine clays related to Lake Warren which existed between 12,500 to 11,500 years B.P.. This was a period of drastic water level drops in both the Erie and Ontario basins following the Port Huron Stadial (Dreimanis and Karrow, 1972).

The subsurface conditions at the site have been investigated by Golder Associates of Mississauga as part of a geotechnical assessment for the construction of the water pumping and filtration plant. Based on observation of auger cuttings and drill core, the site is underlain by 8.5 to 12.5 m. of stiff brown fissured silty clay which overlies a grey, sound to moderately fractured, fine-grained cherty limestone belonging to the Middle Devonian Dundee formation.

Evidence from Shelby tube sampling at the site confirmed the above description and added some interesting detail. The bottom of the last Shelby sample exhibited a coarse-grained and fragmented till with numerous reddish brown clasts identifying it as the Halton till. A near-vertical fracture with a well-developed relic root system was also observed in the same sample.

Essex County Landfill #3

Essex County Landfill #3 is located in Maidstone Township along county road 25 between highways 401 and 2. This area is known as the Essex clay plain and forms part of the St. Clair clay plains physiographic region as described by Chapman and Putnam (1966). The mode of deposition of these clays remains somewhat ambiguous. Lack of stratification tends to exclude a lacustrine origin and a normally consolidated state below a surface crust excludes a lodgement glacial till origin. From borehole logs published by Soderman, Kenney and Loh (1961), the region between Windsor and Tilbury exhibits a 6.6 to 8.2 m. layer of hard to stiff brown clay with high undrained shear strength (190 to 340 kPa), underlain by 23 to 30 m. of medium grey clay with an average undrained shear strength of 0.5 tons/sq.ft. The underlaying bedrock is the Middle Devonian Dundee limestone.

A borehole log for Woodslee, Ontario, located approximately 5 km. southeast of the landfill site, is available (Desaulniers, 1980). Here, the stiff, oxidized clay at surface has a thickness of 4 to 5 m. and the underlying, medium grey, un-oxidized clay terminates at 19.6 m. in a wet sandy silt lens. Drilling and sampling at the landfill to depth of 13 m., confirmed this stratigraphy. No fractures were evident in the deeper Shelby tubes.

City of London Landfill

The City of London landfill is located west of Wellington Rd. south on concession road #7. It was chosen in part because of a distinctly different depositional environment from the other sites. The site is located on the southern flank of the Westminster moraine and consists of Port Stanley silty clay till and clayey silt till deposited by the Erie ice lobe which also produced the Ingersoll moraine to the north and the St. Thomas moraine to the south during the Port Bruce Stadial (Dreimanis, 1964). As described by Chapman and Putnam (1966), Dingman Creek which separates the Ingersoll and Westminster moraines drains a broad valley floored with clay, silt and sand or gravel related to glacial Lake Maumee III. Extensive mapping work has been done by Dreimanis (1964) and he suggests that the Westminster moraine was overridden and is actually older than the Port Stanley till. The fine-textured nature of the Port Stanley till is due to the glaciolacustrine sediments of the Erie Interstadial which were overridden and incorporated by the Erie ice lobe.

The general subsurface conditions at the site were determined by Golder Associates of London, Ontario, as part of a groundwater monitoring program. A borehole located near the present research site identifies a 4 m. thick surface unit of hard brown silty clay till followed by 11 m. of very stiff, grey, silty clay till and finally 10 m. of alternating dense, grey, fine sand and silt layers. Other boreholes also identify a very stiff to hard clayey silt with sand partings below the dense, fine sand and silt unit. This may identify the overridden Westminster moraine as postulated by Dreimanis. Shelby tube samples collected for the present study confirm the above stratigraphy to a maximum borehole depth of 13.5 m. The underlying bedrock at the site is the Middle Devonian Dundee limestone.

MECHANISMS OF FRACTURE FORMATION IN SOUTHWESTERN ONTARIO

Desiccation

Desiccation is a process of dehydration of soil through evaporation and water table lowering. As the pore water pressure decreases to zero and then into the negative range, the effective stress increases following the well known Terzaghi relationship. This causes the soil to consolidate and generates horizontal shrinkage stresses (tensile) as described by Blight and Williams (1971). The relief of these horizontal shrinkage stresses produces surface cracks through the release of accumulated strain energy. The fracture pattern initiated in an intact soil will tend to form so that a minimum of crack surface will relieve a maximum amount of strain energy per unit volume. As stated in Blight and Williams (1971) and Price (1966), a hexagonal fracture pattern meets this requirement most effectively and is the most common pattern noted in dehydrated muds. This pattern of vertical to sub-vertical fractures would produce a lower-hemisphere equal-area stereonet with plotted poles appearing randomly distributed around the stereonet periphery. Using the fabric classification developed by Fookes and Deness (1969), the desiccation fracture pattern would be classified as a major girdle normal to ground surface.

Shearing

A shear mechanism of fracture formation, in a southwestern Ontario context, could be produced by glaciers overriding pre-existing clay deposits. The direction of ice advance, being the direction of maximum principal stress, would be oriented such as to bisect the acute angle of intersection of developed shear planes. The fracture surfaces would be slickenslided due to reorientation of clay particles in the direction of shear.

Fookes (1965) observed that low-angle shear planes in the overconsolidated Siwalik clays of West Pakistan have slickenslided surfaces that are oriented parallel to sub-parallel to a large surface shear zone. Some shear planes parallel to bedding and are considered flexural-slip shears developed by bed slippage during folding of the bedrock. This type of shear mechanism would not be present at the sites investigated for this paper.

Stress Relief

Stress relief is a phenomenon by which vertical stresses are reduced by either removal of overburden through erosion or removal of glacial ice load through deglaciation. In both cases, the underlying clay deposits would exhibit some degree of overconsolidation with respect to the present ground surface. The mechanism of fracture formation in this case would be dilation of the clay beds due to unloading. Fookes and Deness (1969) concluded from their study of Cretaceous sediments of south-east England, that stress release normal to ground surface did not have a direct influence on fracture formation much below a depth of one metre. However, if bedding were also parallel to ground surface, then one could expect the formation of uni-planar fractures parallel to bedding. A lower-hemisphere equal-area stereonet would show a pole concentration near its centre.

During deglaciation, the major principal stress may be rotated into the horizontal plane and the minor principal stress into the vertical plane. If the horizontal stresses are large enough to generate local failure in compression, the shear planes would be produced at very low inclinations related to the materials internal friction angle.

Tectonism

In southwestern Ontario, tectonic forces have influenced the underlying bedrock and are still active today as evidenced by numerous earthquake epicentres (Sanford, Thompson and McFall, 1985). It seem reasonable to suggest that in areas of shallow overburden, tectonic stresses and related block fault movements would affect fracture patterns of the surface clay deposits. Kendall and Briggs (1933) suggested that joints were fatigue phenomenon and resulted from alternating, regularly oriented torsional stresses produced by semi-diurnal rock tides generated by the gravitational attraction of the moon. They concluded that joints developed early in the history of sediments and were a result of minute, rhythmic, differential movements along joint planes which pre-existed in more competent sediments. These movements would in time result in the upward propagation of joint planes into the overlying unconsolidated sediments.

Analytical and experimental work done by Sanford (1959) examined the elastic response of a homogeneous rock layer to two-dimensional distributions of vertical displacement applied along a lower boundary. In the case of a step-like vertical displacement, such as would occur during faulting of a basement complex, curved shear planes developed immediately above the fault line in the basement. Horizontal tensile stresses were also produced near the upper surface on the uplift side of the fault. Tension fractures produced in this way would exhibit a strike direction similar to the fault line and have a vertical to sub-vertical dip. An application of Sanford's analytical model to a normally-consolidated clay layer overlying bedrock may determine the extent and magnitude of tensile stresses generated at the surface and the possibility of fracture formation in this way.

Syneresis

White (1961) reported laboratory test results on clay mineral suspensions and concluded that syneresis cracks were fissures that developed in a suspension as water was expelled from the clay/water system by internal forces. Cracks within the suspension would have a completely random orientation from vertical to horizontal directions and shrinkage would therefore occur in all directions. This type of mechanism would take place shortly after deposition of the clays and would be dependent on the chemistry of the depositional environment. Mud cracks in present day sediments may be a result of syneresis. A lower-hemisphere equal-area stereonet representing syneresis cracks would exhibit a completely random orientation of strike and dip.

FRACTURE MAPPING METHODOLOGY

Trench Geometry and Shoring

Near-surface fracture mapping was accomplished within a shallow trench dug by a backhoe or excavator. The design requirements for the trench were determined from consulting the Ontario Ministry of Labour's "Occupational Health and Safety Act and Regulations for Construction Projects", and from discussions with representatives of the Kitchener district office. The trench design involved the following:

1) The top 1.2 meters (4 feet) sloped with a gradient of 1:1, followed by 2.7 meters (9 feet) of braced vertical wall for a total depth of 3.9 meters (13 feet).
2) An hydraulic bracing system manufactured as SPEEDSHORE was used for supporting the vertical portion of the trench. Four sets were placed at 4-foot centers as required for the soil type #2 encountered at all the sites. In a plan view, the vertical portion of the trench was 3.6 meters (12 feet) long and 1.5 to 1.8 meters (5 to 6 feet) wide.
3) Within the 1.2 m. deep, sloped portion of the trench, a 60 cm. bench was cut thereby permitting fracture mapping and sampling near the surface.

Measurement Technique

The fractures in the clay were mapped within 60 cm. intervals between the Speedshore sets. In general, two entire sections along both long walls of the trench were mapped as well as the exposed areas of one end wall. It was hoped that in this manner all the possible fracture sets would be represented.

The fracture mapping was a slow and tedious process because the surfaces of the trench walls were smeared by the backhoe bucket during excavation. The individual fracture planes had to be "found" by digging into the clay walls with a soil trowel and their strike and dip measured using a Brunton compass and inclinometer. This may have produced a data bias since the fractures mapped were those easily found and recognized. Fractures in the overconsolidated Cretaceous and Early Tertiary sediments of southeast England have been extensively mapped and analyzed by workers such as Fookes and Deness (1969), Fookes and Parrish (1969) and Skempton, Schuster and Petley (1969). In these cases, all the fractures were readily visible along exposure surfaces much like those in bedrock.

Bag sampling for mineralogical analysis began at a depth of 75 cm. and proceeded down the trench wall at 30 cm. intervals. The coating on fracture walls was also sampled for X-ray diffraction analysis. Block sampling was attempted at specific depths within the trench and each block was wrapped in plastic followed by 2 to 3 layers of cheesecloth and microcrystalline wax.

Some Problems Encountered

Upon completion of the excavations at all three sites, it was observed that the vertical section exposed between 60 cm. and 1.2 m. below ground surface was so heavily weathered and indurated that fracture mapping and block sampling within this interval would be extremely difficult. It was decided that the upper 1.2 m. of the section would be ignored and that the remainder would be mapped in 60 cm. intervals between the SPEEDSHORE sets.

The upper clay at Essex was very stiff and highly fractured. This made it difficult for the backhoe operator to produce a straight and smooth trench wall, making the installation of shoring very time consuming. The use of a heavier excavation machine at the London site produced better results in an equally stiff and fractured material.

The problem of water seepage into the trenches was evident at all three sites and was most serious at the Essex site due to recent heavy rainfall and a location near a topographic low. It is also suspected that old drainage tiles still in the field may have aggravated the problem. However, since the trenches were to be left open for a maximum of 2 to 3 days, the only major consequences of water accumulation were lost footing and an inability to block sample at the trench bottom.

Block sampling from the trench walls at all three sites proved difficult due to the close spacing of fractures at the surface and the occurence of dominant fracture sets parallel to the trench long walls. In almost all cases, the process of digging out a large block sample (30 cm.to a side) caused opening of the fractures and breakage of the block. Sampling at the Nanticoke site was restricted to previously failed blocks, and at the Essex site to blocks 15 cm. to a side. The London site provided the only large intact block sample taken from an end wall.

The measurement of fracture spacing was abandonned because not all the members of a particular fracture set could be exposed for measurement. This made the spacing values rather meaningless. A qualitative description of fracture spacing was obtained.

FRACTURE MAPPING RESULTS

The fracture mapping data given in terms of strike and dip directions are presented and analyzed using three graphical methods: lower hemisphere, equal-area projection, frequency distribution of strike directions or rose diagrams and a histogram of dip angles.

Priest (1985) points out that the hemispherical projection method can be inaccurate but that in his experience, results within 2 degrees of the correct orientation can be obtained consistently. This precision is adequate for most rock mechanics work since natural discontinuities are rarely planar throughout a rock mass and that their orientations, as measured in the field, will usually be distributed widely about a mean value. This statement is quite valid for soils as well, especially in the context of this research where most fracture planes could only be exposed over small areas due to their short spacing. Therefore, small orientation changes within a given plane could rarely be detected and taken into account.

The use of an equal-area equatorial net is recommended when interpreting and analyzing plots of fracture plane normals because of a lack of areal distortion (Priest, 1985). All hemispherical projections in this study have therefore been done on equal-area or Schmidt nets.

Nanticoke

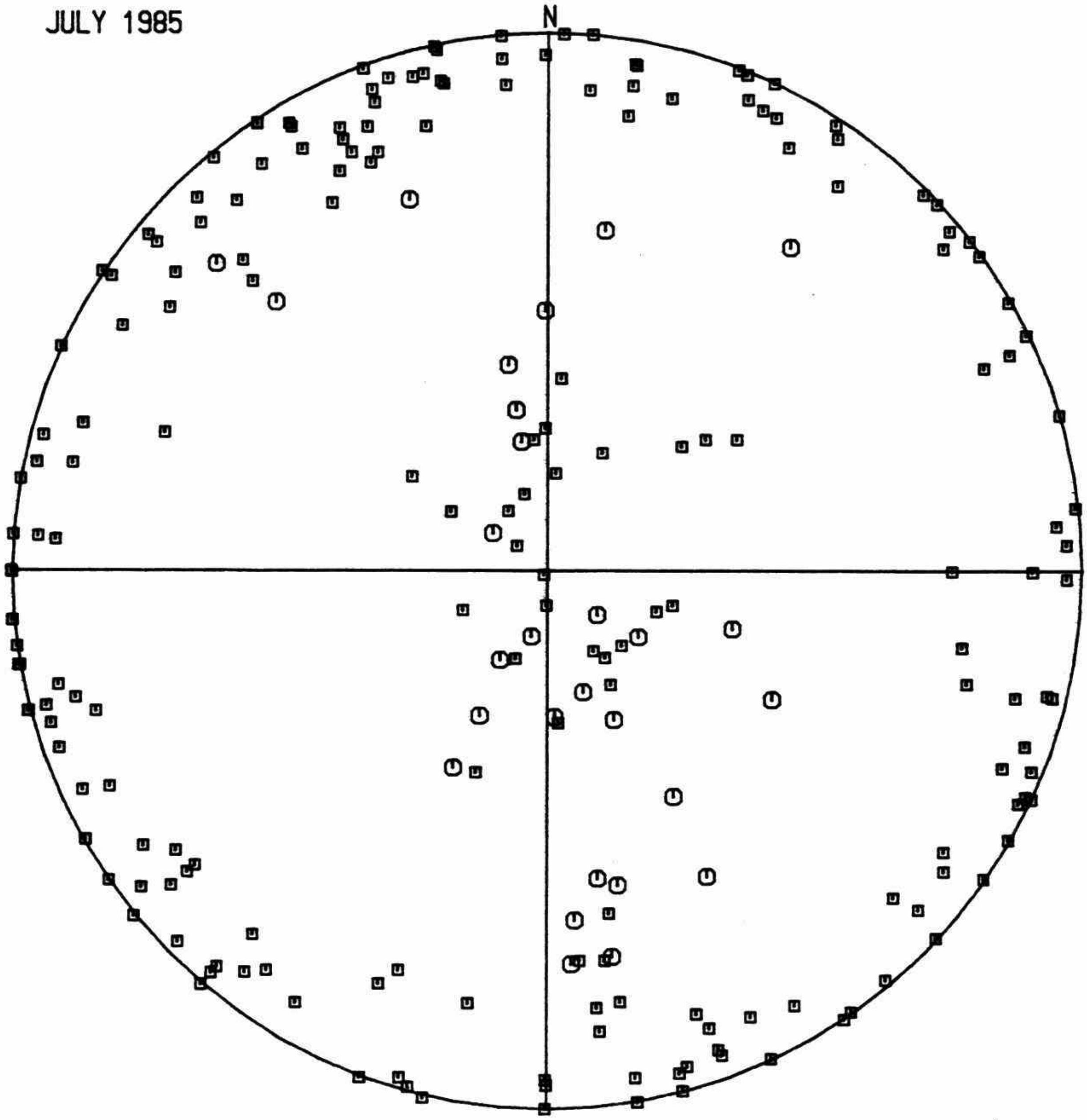
Three families of fractures were observed at the Nanticoke site. A vertical to sub-vertical, random set of fractures was observed with the following distinctive features: a light-grey, very fine-grained fracture coating, a discolouration halo 5 to 15 mm. wide progressing from light brown at the fracture to medium brown and into the dark brown of the surrounding matrix. These identifying features were also associated with individual root holes. These alteration products could be a function of weathering and groundwater flow through this glaciolacustrine deposit. In the fracture planes themselves, numerous rootlets and root impressions were found, even in the Shelby tube samples collected from a depth of 10 m.. This would indicate that the permeability of the fractures was relatively high in the past.

A second set of shallow dipping fractures strike in an east-west direction, parallel to the trench long wall. This set of fractures was the main contributor to instability of the trench walls. These fracture planes are undulating and exhibit clear slickenslided surfaces indicating that some relative movement had taken place along them, in the direction of dip.

A third set of fractures are horizontal to sub-horizontal and are clearly related to the varving of this deposit, being coated by very fine silt particles. It is not yet clear whether these planes are inherently weak due to the silty coating or if they were produced by some stress relief mechanism

The equal-area stereonet projection shown in Figure 2 confirms the initial observations made in the field. However, the shallow dipping fractures range in dip from 10 to 80 degrees from horizontal and there appears to be a preferred concentration of poles (normals) in the north-northwest section of the diagram. The rose diagram shown in Figure 3, confirms the dominance of this fracture set within the 70 to 90 degree azimuth range. Four other strike directions are significant and they are the following: 10 to 20, 30 to 50, 110 to 120 and 140 to 150.

The histogram of dip angles shown in Figure 4 shows two peaks: an 8% peak between 10 and 20 degrees and a 50% peak between 80 and 90 degrees. Approximately 70% of the dip angles



FRACTURE ORIENTATIONS

NANTICOKE

JULY 1985

LEGEND :

▪ ALL FRACTURES FROM NANTICOKE TRENCH

● SLICKENSLIDES FROM NANTICOKE TRENCH

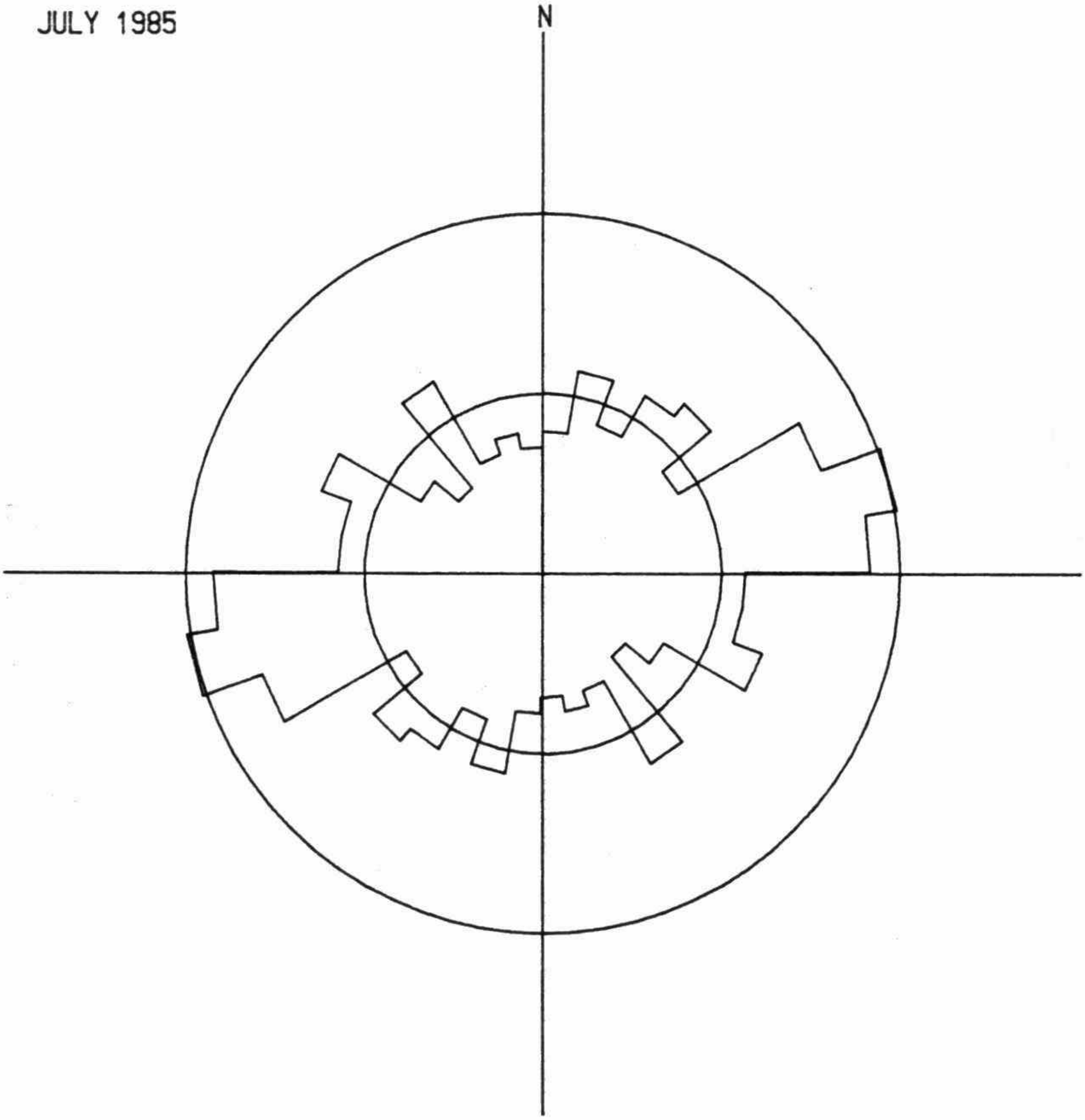
Figure 2

EQUAL-AREA STEREONET PROJECTION

FRACTURE ORIENTATIONS

NANTICOKE

JULY 1985



5% AND 10% CIRCLES ARE DRAWN

228 OBSERVATIONS HAVE BEEN PLOTTED

Figure 3
ROSE DIAGRAM OF STRIKE DIRECTIONS

FRACTURE ORIENTATIONS

NANTICOKE

JULY 1985

HISTOGRAM OF DIP ANGLES

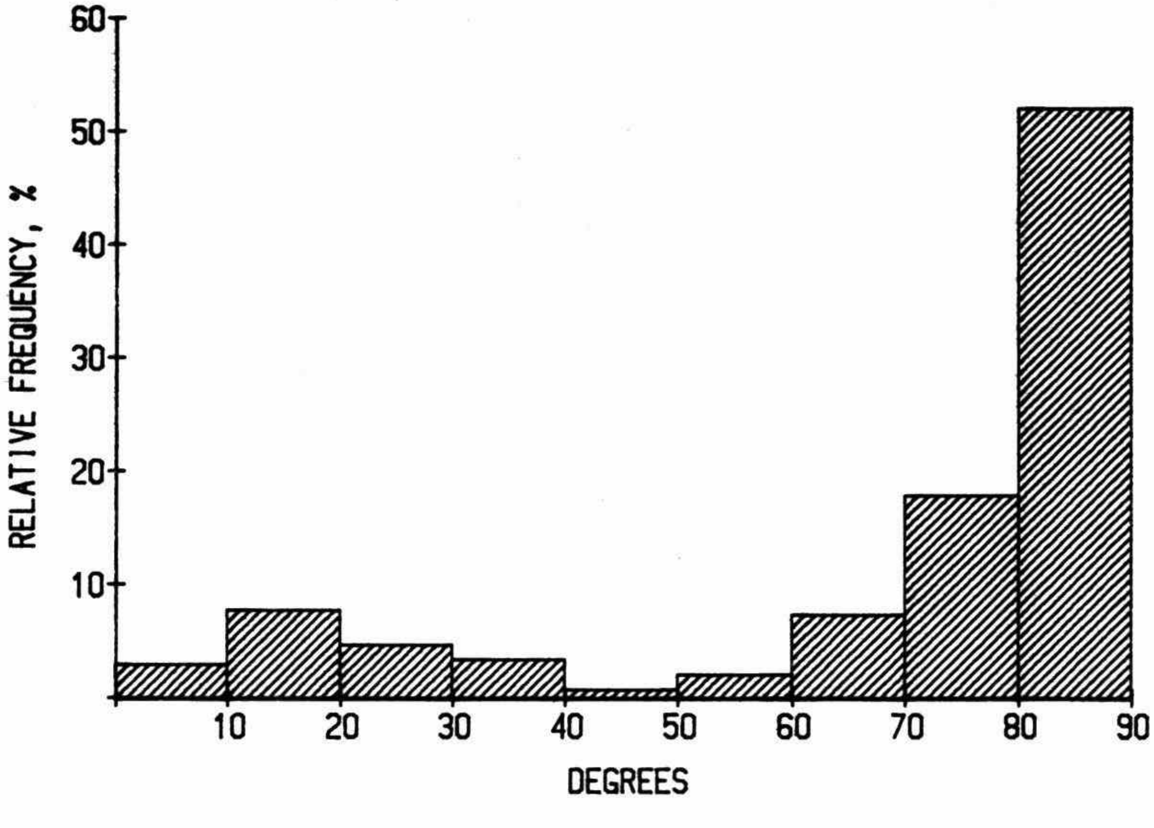


Figure 4

range between 70 and 90 degrees.

Essex

Fracture mapping at Essex County Landfill #3 was considerably more difficult due to the higher degree of chemical and physical weathering near the surface of the clayey till deposit. The light brown clayey matrix was very stiff to hard and excavation with a backhoe could not extend beyond a depth of 4 m.. Vertical to sub-vertical fractures with an apparently random strike are the dominant set observed. Fracture plane coating, discolouration, root and root impressions, are similar to those observed at Nanticoke; however, on the fracture planes below 3 m., black streaks of iron or manganese salts as well as iron oxide staining are more apparent. Blight and Williams (1971) and Burford and Dixon (1978) obverved similar features in the clays of South Africa and northern Ohio respectively.

The equal-area stereonet projection of all the data, shown in Figure 5, confirms the random distribution of near-vertical fractures at the site, but also indicates a concentration of poles in the northeast quadrant. No bedding features were observed along the trench walls, therefore the shallow dipping planes represented in the stereonet may have been produced by some stress relief mechanism.

The rose diagram shown in Figure 6 confirms the dominance of fractures striking in the northwest and southeast quadrants. No dominant set is evident but rather a wide distribution of strikes centered on the 140 to 150 degree interval. Other individual fracture sets are difficult to identify due to their random distribution, but an east-west striking set does appear significant.

The histogram of dip angles (Figure 7) shows that over 70% of the fractures recorded had dips ranging from 80 to 90 degrees. This factor, plus the close spacing of the fractures near surface, suggest that the trench would be unstable but in fact the walls remained intact for a period of 15 hours between removal of the shoring and backfilling.

London

The long walls of the trench at the City of London Landfill were the only ones oriented in a north-south direction. The fracture coatings and discolouration halos were similar to those found at Essex, with black streaks and root holes found to a maximum depth of 4 m.

From the stereonet projection shown in Figure 8, it is evident that the intensity of fracturing is much greater at the London site than at Essex or Nanticoke, due to the fact that this clay till deposit has been exposed to weathering for a couple of thousand years more than the other deposits. However, the trench walls remained stable through the mapping period and no seepage faces became evident. The vertical to near-vertical fractures seem randomly distributed about the stereonet periphery but do show a concentration of poles in the east-northeast, west-southwest sections. Some of the low-angle dipping planes show

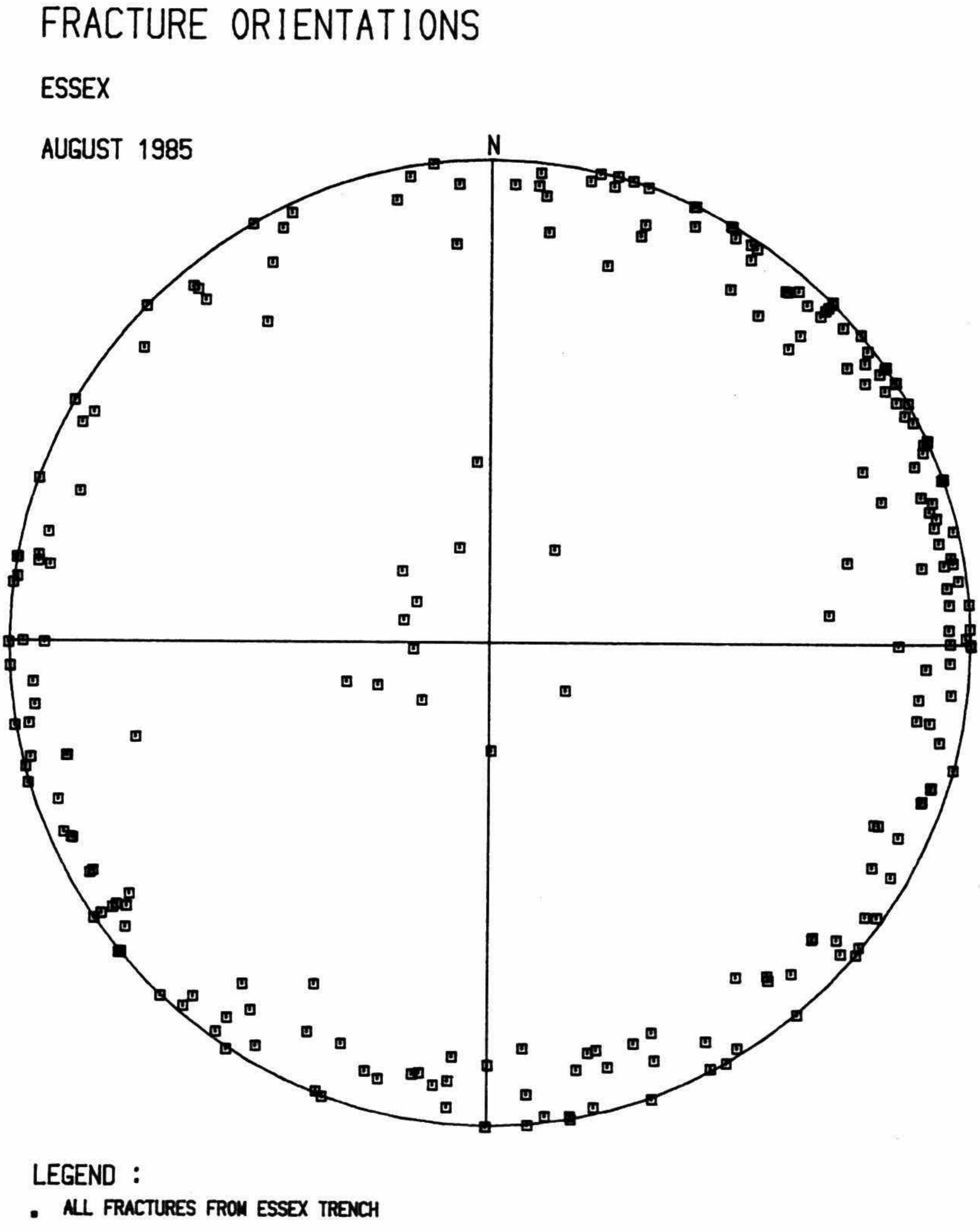


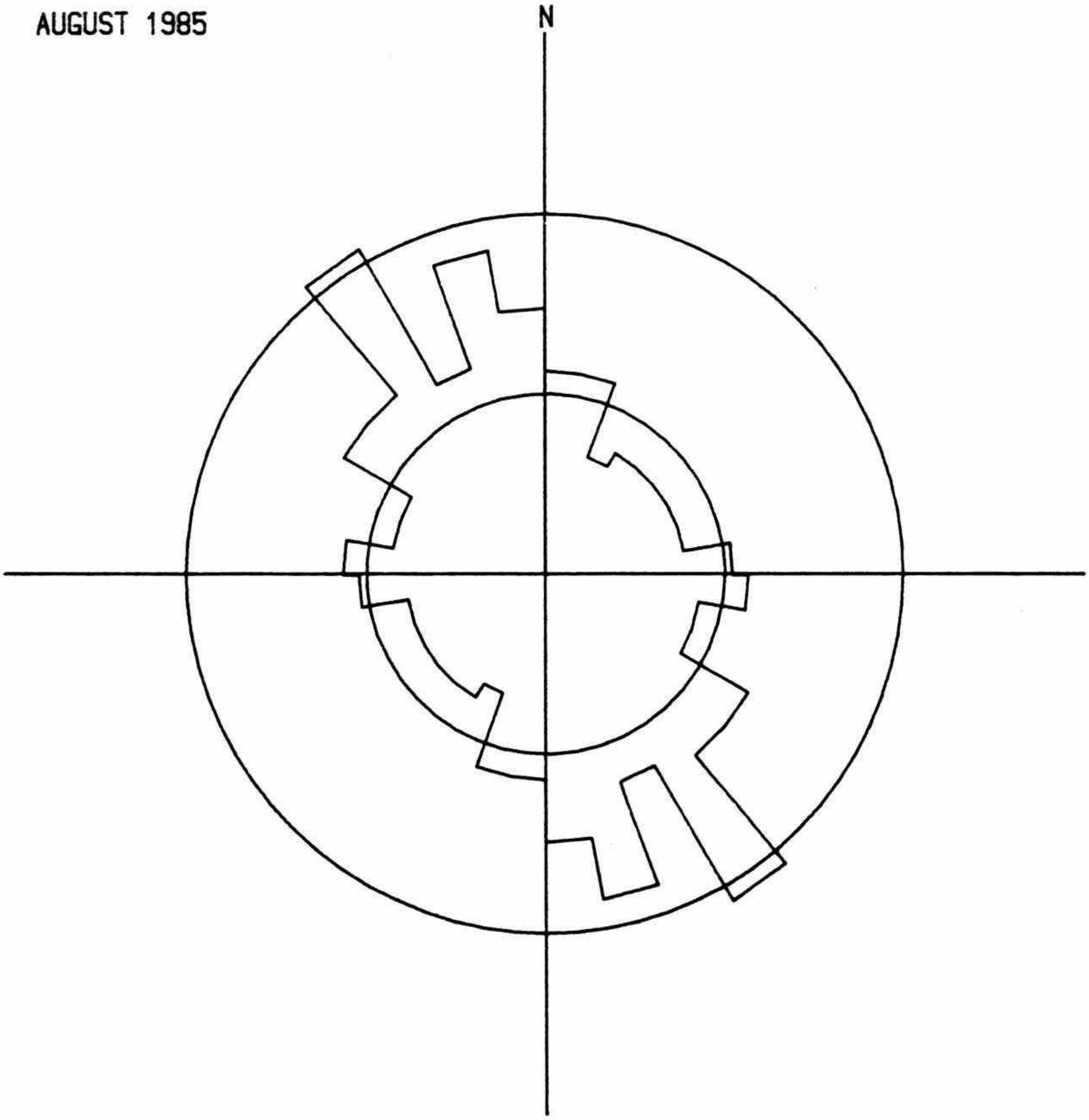
Figure 5

EQUAL-AREA STEREONET PROJECTION

FRACTURE ORIENTATIONS

ESSEX

AUGUST 1985



5% AND 10% CIRCLES ARE DRAWN

230 OBSERVATIONS HAVE BEEN PLOTTED

Figure 6
ROSE DIAGRAM OF STRIKE DIRECTIONS

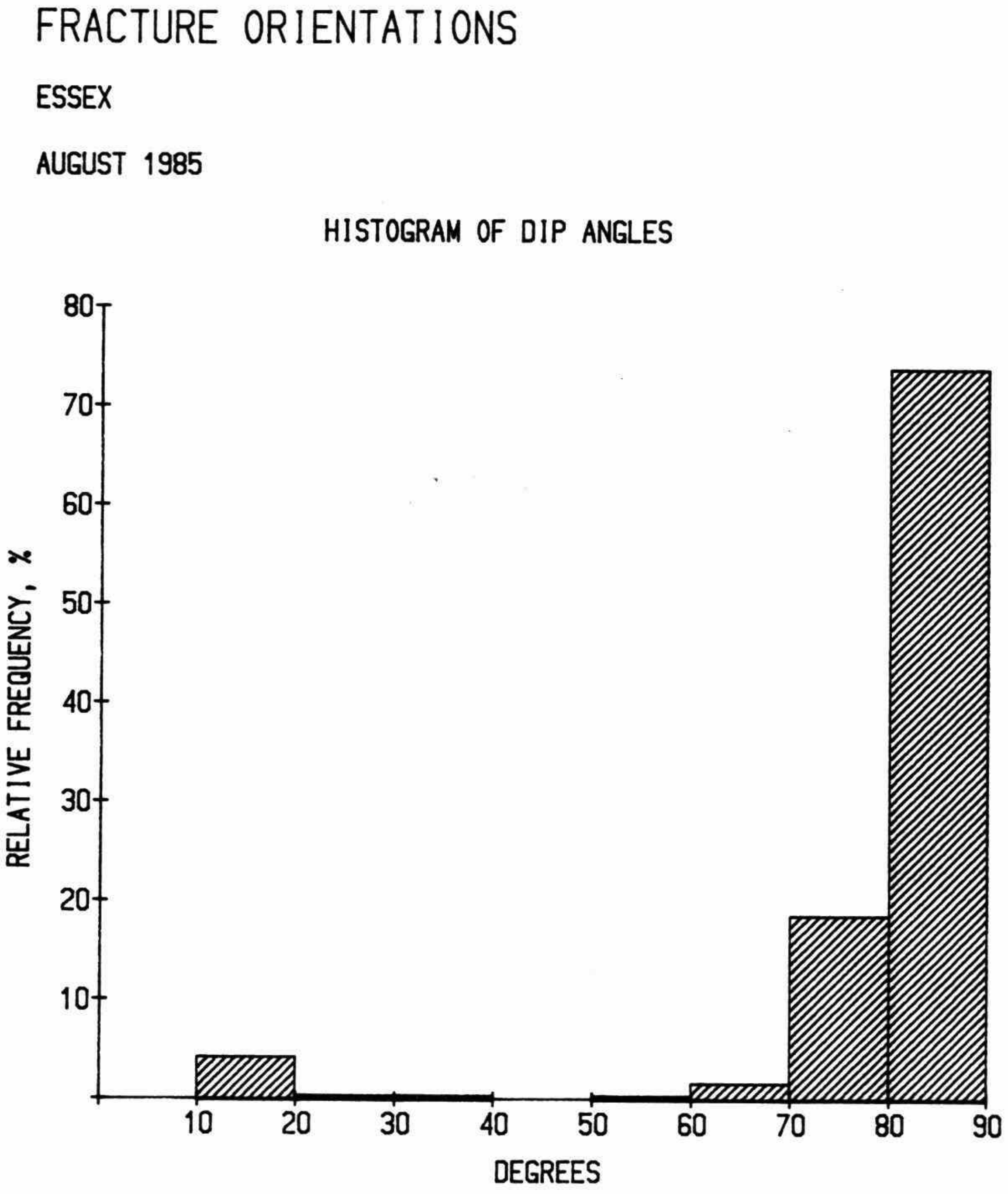
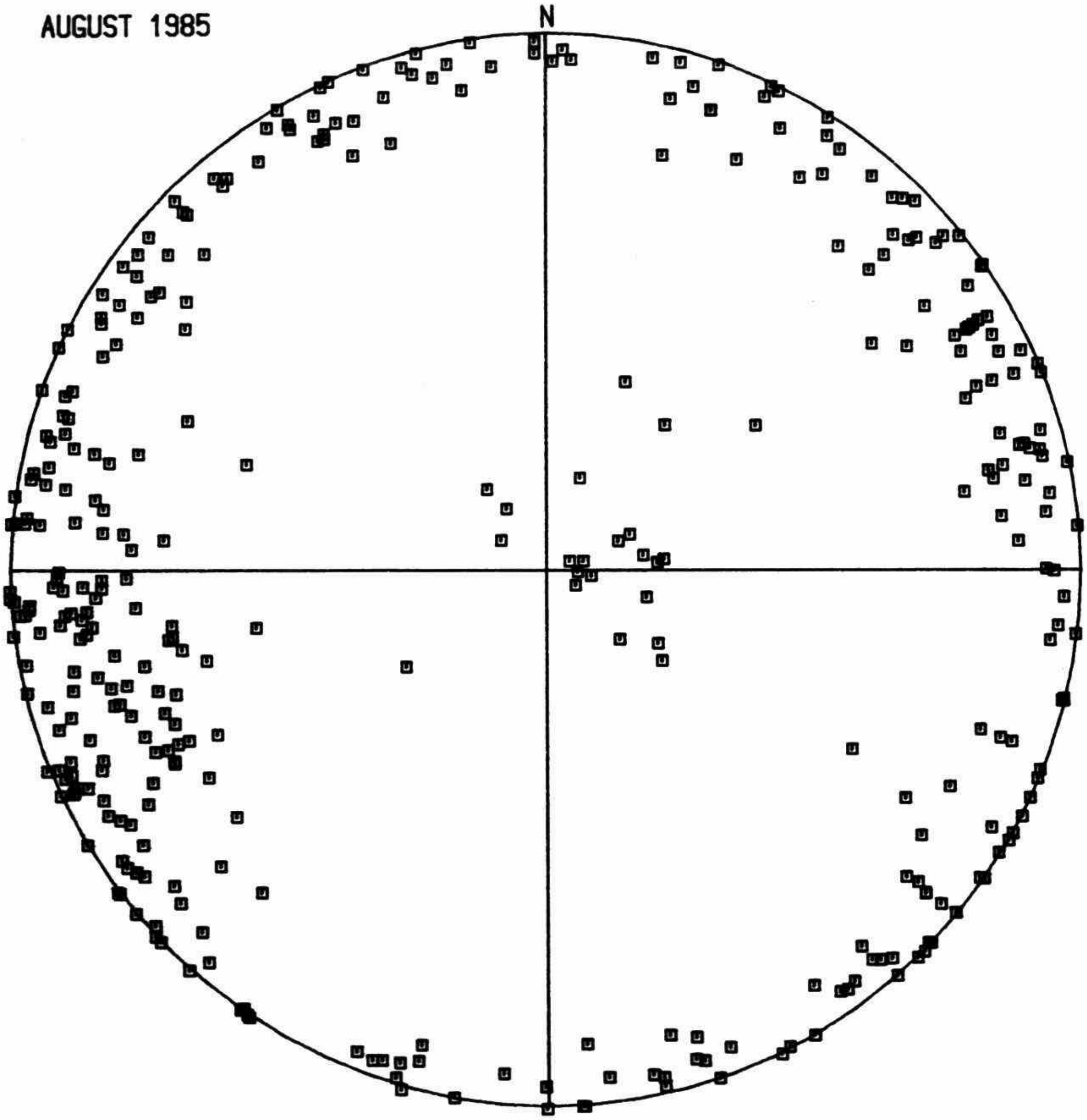

FRACTURE ORIENTATIONS
ESSEX
AUGUST 1985
HISTOGRAM OF DIP ANGLES
RELATIVE FREQUENCY, %
80
70
60
50
40
30
20
10
10
20
30
40
50
60
70
80
90
DEGREES

Figure 7

FRACTURE ORIENTATIONS

LONDON

AUGUST 1985



LEGEND :

▪ ALL FRACTURES FROM LONDON TRENCH

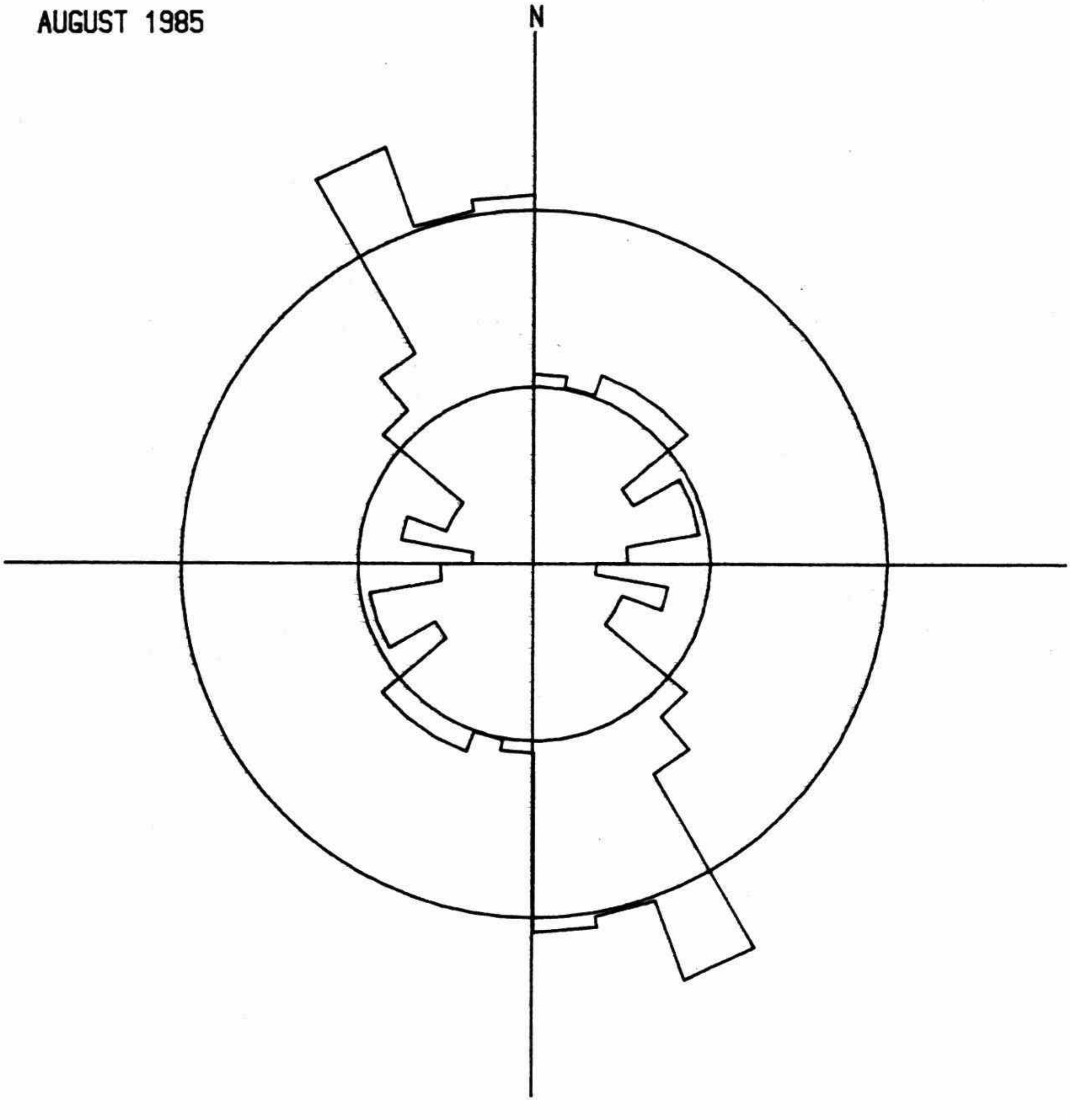
Figure 8

EQUAL-AREA STEREONET PROJECTION

FRACTURE ORIENTATIONS

LONDON

AUGUST 1985



5% AND 10% CIRCLES ARE DRAWN

336 OBSERVATIONS HAVE BEEN PLOTTED

Figure 9

ROSE DIAGRAM OF STRIKE DIRECTIONS

FRACTURE ORIENTATIONS

LONDON

AUGUST 1985

HISTOGRAM OF DIP ANGLES

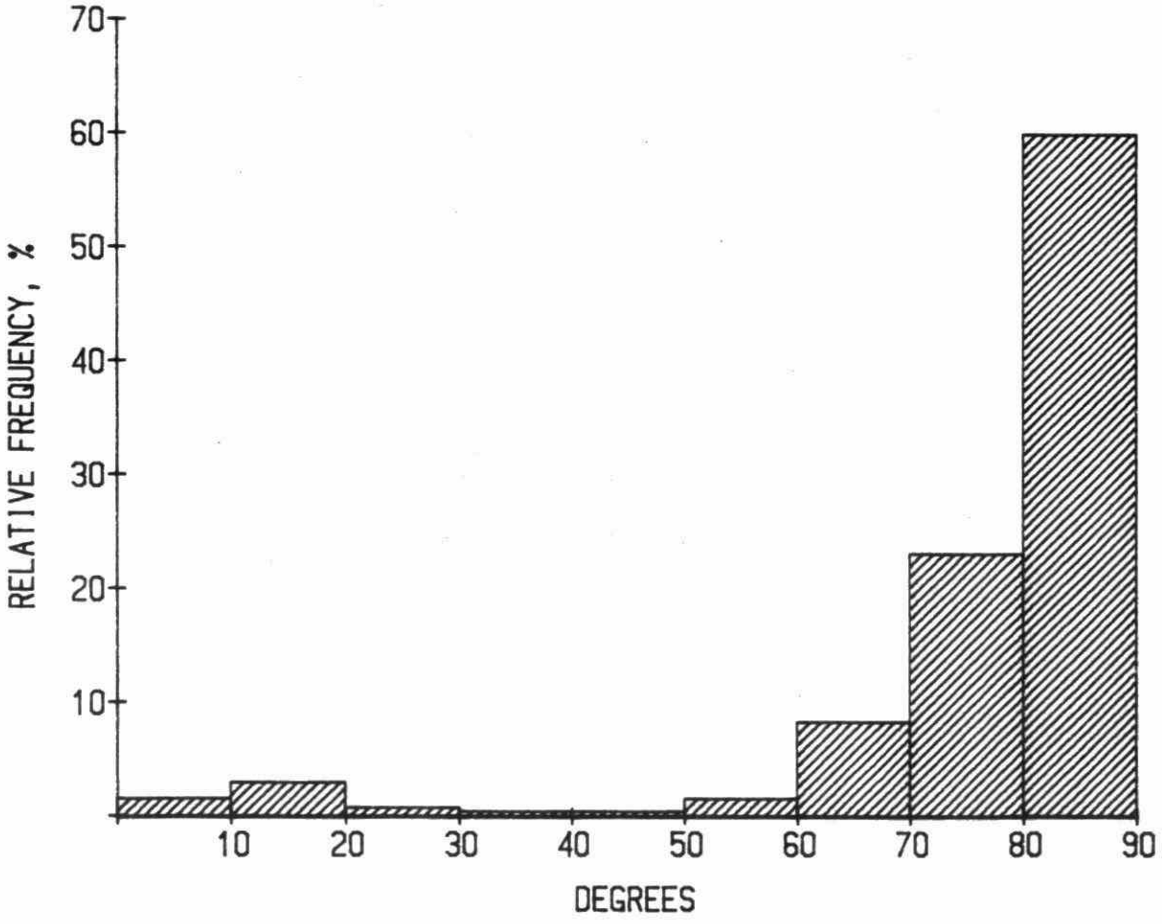


Figure 10

remnants of slickenslides which have since been obscured by weathering.

The rose diagram in Figure 9 clearly shows a preferred direction of strike within the 150 to 180 degree intervals. This preferred orientation is very similar to that shown by the Essex rose diagram, however the two sites are located in geographically and morphologically different areas. Other important fracture sets are within the following intervals : 20 to 50, 60 to 80 and 100 to 110 degrees.

The histogram of dip angles in Figure 10, illustrates that over 80% of the fractures observed were dipping 70 to 90 degrees from horizontal.

INTERPRETATION OF RESULTS

Before the plotting and analysis of the fracture orientation data collected from the Nanticoke, Essex and London field sites, it was assumed that the fracture patterns at all three locations would exhibit a random distribution. This is clearly not the case as shown by the rose diagrams previously discussed. Aside from the characterization of the dominant fracture trends in the near-surface clays and clay tills examined, another purpose of this phase of the research is to attempt to identify the fracture mechanisms which have affected these deposits.

From an analysis of the orientation data, it can be concluded that several fracturing mechanisms have been superimposed on the same deposit thereby excluding a straightforward analysis. By coupling orientation data with the geologic history of these deposits an interpretation of the possible fracture mechanisms will be attempted.

It seems reasonable to assume that desiccation has been one of the dominant mechanisms acting upon the surface clays and clay tills. As previously discussed, the most likely fracture pattern produced by desiccation would be that of a hexagon, or three dominant fracture sets with acute angles of intersection close to 60 degrees and dips close to vertical. None of the fracture patterns shown in the stereonets exhibit this ideal distribution, perhaps due to small heterogeneities in the clay matrix. Dehydration of the surface clays would be anisotropic, rather than isotropic, due to water loss at the water table surface by upward moisture migration along the capillary tubes of the soil as suggested by Soderman and Kim (1970). Also, the orientation of a fracture mapping face within a pseudo-hexagonal fracture pattern may lead to the dominance or abscence of specific directions. It is most important then, that two orthogonal faces be mapped to insure the presence of all fracture sets. This has been done in this survey.

Minor fracture sets illustrated in the rose diagrams of all three sites are probably associated with desiccation and volumetric shrinkage. This implies that at the time of formation these fractures were open, allowing the migration of surface waters and groundwaters leading to alteration of the fracture walls. These minor patterns have been superimposed on a strong preferred orientation of strike at Nanticoke, Essex and London.

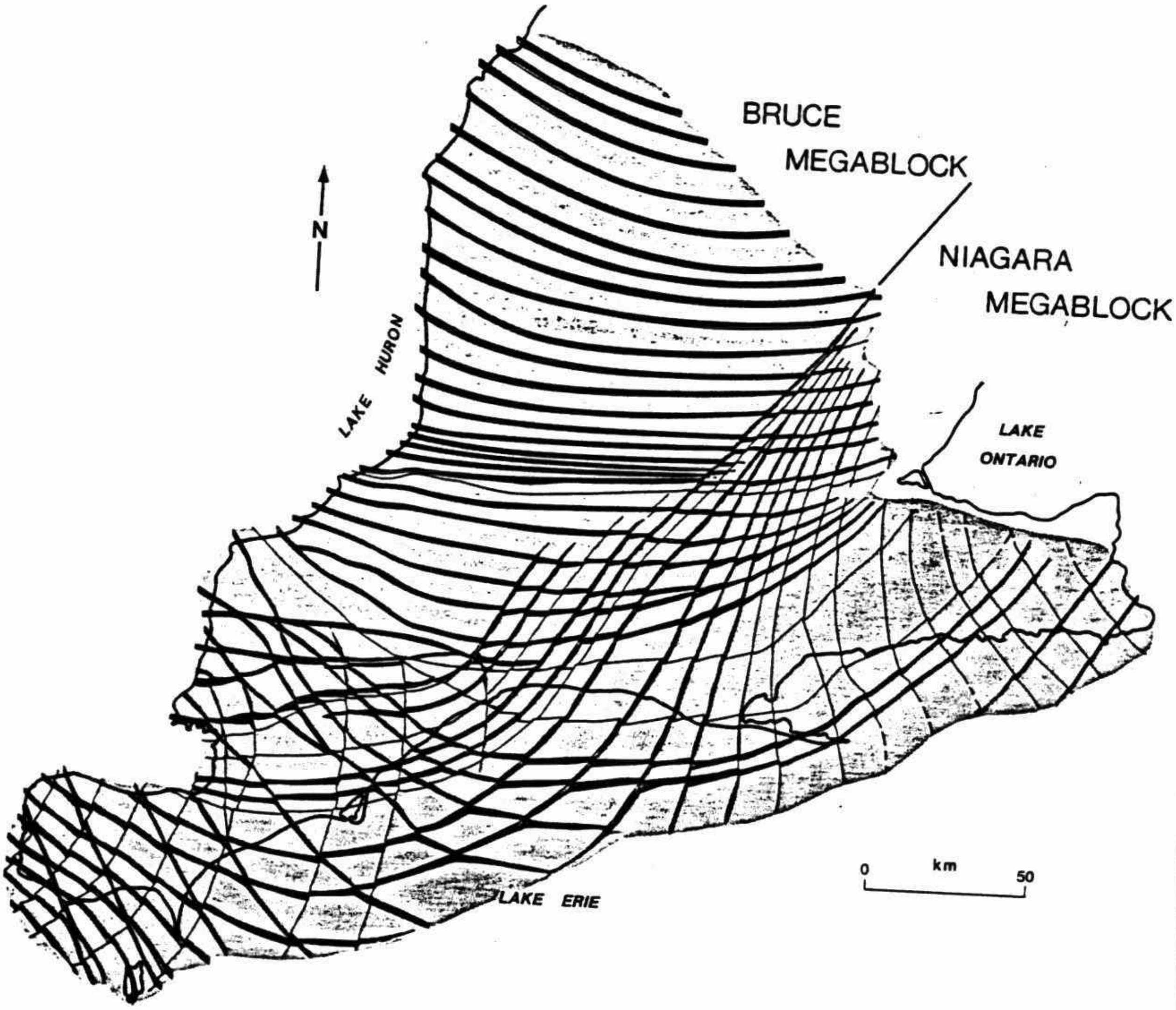
The first step taken to insure the authenticity of these preferred directions was to plot the data for each individual trench wall. In almost every case, the dominant directions of strike for the total data sets were also dominant in the individual wall plots. Most of the minor sets were also reflected in the individual plots, however not to the same degree due to the different number of observations made and the different orientations of the mapping face. The question still remains than, what type of fracture mechanisms could have produced a strong preferred direction of strike? A look at the geographical settings of each site may provide some possible answers.

The London site is located on the southern flank of the overridden Westminster moraine. Upon retreat of the Erie ice lobe during the Mackinaw Interstadial, a mechanism of hill creep triggered by stress relief may have produced fracture sets conforming to the direction of slope and contour of the topography. This phenomenon is stated in Price (1966) for igneous and sedimentary rock sheets subjected to downhill sliding in response to gravity. The local stresses induced by hill creep may have lead to the formation of preferentially oriented desiccation fractures.

The Nanticoke site possesses some interesting features which make a certain type of fracture mechanism very attractive. The clayey deposit is approximately 10 to 12 m. thick and directly overlies the Dundee formation limestone. Well developed fractures have been observed in Shelby tube samples from a depth of 10 m.. This suggests that bedrock joints have been propagated upwards into the unconsolidated sediments as suggested by Burford and Dixon (1978), who described systematic fracturing in lacustrine clays overlying Upper Devonian shales and sandstones in Ohio. The possible mechanism for this propagation has been previously discussed in a subsection on tectonism.

It is interesting to note that in Sanford, Thompson and McFall (1985), a conceptual fracture framework for southwestern Ontario has been developed. It is based on contour, isopach and facies maps for the Middle Silurian Rochester shale as this horizon is a reliable subsurface formation pick for fracture mapping purposes. Underlying the Nanticoke area, the orientation of one of the fracture sets in the Rochester shale roughly parallels the preferred strike direction shown in the Nanticoke rose diagram (Figure 11). Sanford, Thompson and McFall (1985) state that the rocks of the Dundee Formation have been deformed as a result of selective dissolution of the underlying Salina salt along rejuvenated fractures. This deformation of the Dundee may have led to fracturing in the overlying unconsolidated sediments.

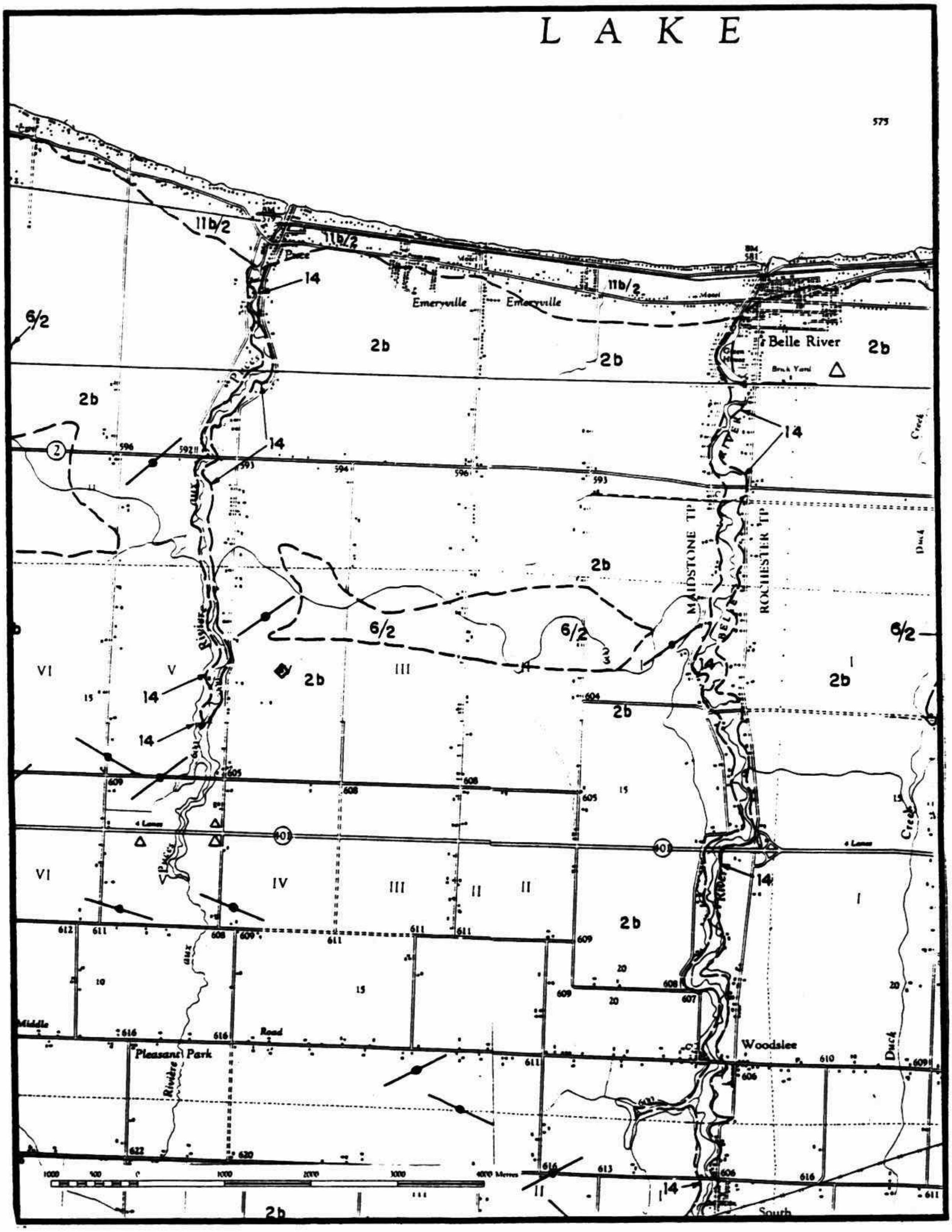
The preferred orientation shown by the Essex fracture data is much more difficult to explain. The site is located in a region of flat topography and the clayey deposit is approximately 30 m. thick overlying the Dundee Formation limestone. Eventhough the preferred orientation of surface fracturing parallels another major fracture set in the underlying bedrock (Sanford, Thompson and McFall, 1985), there were no fractures found in the Shelby tube samples collected from a 13 m. depth.



CONCEPTUAL FRACTURE FRAMEWORK, SOUTHWESTERN ONTARIO

(SANFORD, THOMPSON AND McFALL, 1985)

Figure 11



QUATERNARY GEOLOGY OF THE BELLE RIVER AREA (VAGNERS, 1972)

2b - CLAYEY SILT TILL

6/2 - TILL AND THIN COVER OF GLACIOLACUSTRINE MEDIUM SAND

14 - UNSUBDIVIDED MODERN ALLUVIUM

◆ - ESSEX SITE LOCATION

Figure 12

The major and minor drainage patterns along the south shore of Lake St. Clair are in a north-south direction with minor deviations in north-northwest and north-northeast directions (Figure 12). This pattern is roughly mimicked in the Essex rose diagram. Since Lake St. Clair to the north of the site dominates the direction of surface and subsurface flow, this may have affected the formation of near-surface fractures in the clayey sediments.

CONCLUSION

Desiccation, topography, drainage direction and proximity to bedrock have been suggested as possible influences on near-surface fracture patterns in clayey sediments. More field work is required in different areas of southern Ontario to investigate the types of fracture patterns and fracture mechanisms. It is clear from the data presented that more than one mechanism of fracture formation may have affected the area, as also concluded by Burford and Dixon (1978).

An appreciation for the various fracture-forming mechanisms in southwestern Ontario may lead to a first approximation of dominant fracture patterns in specific areas.

ACKNOWLEDGEMENTS

This research has been funded by an Ontario Ministry of the Environment Research Grant RAC 147 PL. We also wish to thank Mr. B. Pett, supervisor at the Nanticoke Water Pumping Station, Mr. J. Mullins, supervisor of Essex County Landfill #3 and Mr. Choma, environmental engineer for the City of London, for the helpful cooperation in allowing site access and providing site investigation reports. We also wish to thank Jim Wong and Sam Vales for their assistance during the field work.

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WASTE MANAGEMENT PLANNING FOR THE PHARMACEUTICAL INDUSTRY

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Key words: Waste Management, Pharmaceutical Waste, Waste Disposal.

ABSTRACT

Information obtained on the subject study will be thoroughly reviewed. A questionnaire will be prepared and sent to all pharmaceutical manufacturers in Ontario.

The questionnaire will be based on the types of drugs produced, processes used, chemical or raw materials used, solid and liquid waste produced. There will be questions on the type of wastes (for classification purposes), quantities produced and present methods of disposal (e.g. treatment facility, handlers, disposal companies). There will also be questions concerning the hazardous nature of wastes, chemical analysis, inventory labelling, storage, etc.

Once the questionnaires are mailed, personal interviews will be arranged with the companies who do not respond within a definite time, to obtain first-hand information (and perhaps to explain the questionnaire if not properly understood, its purpose, etc.).

During 1984-85, the main thrust will be to obtain maximum information through interviews and the questionnaire, to establish a data base, inventory requirements and approaches, and also to document regulatory policies and requirements pertaining to the industry.

This paper outlines our plans for the study, with emphasis on the work of the fiscal year 1985-86. The first objective is to assess present practice in the pharmaceutical industry in Ontario, in the disposal of wastes of all kinds. These will include unwanted by-products, off-specification products and intermediates, and laboratory wastes. The aim is to determine the types and quantities of wastes, the kinds and degrees of hazard they represent, and their potential environmental impacts, in the context of the present laws and regulations concerning their storage, handling, transportation and disposal. The final report will include a comprehensive waste management plan.

We are now in the process of preparing a questionnaire, which will be mailed mainly to manufacturers (See Table 1), but also to some packagers and distributors, in order to obtain a better understanding of the types and quantities of wastes generated. This questionnaire covers the following areas:

a) The types of pharmaceutical products handled, whether manufactured, compounded, packaged, distributed or utilized, at any particular site.

b) For each class of pharmaceuticals listed in Table II,

    (i) the typical quantity requiring disposal annually/monthly/weekly,

    (ii) the names of those substances requiring disposal which are classified as liquid industrial or hazardous wastes under Schedules 2A and 2B of Regulation 309.

    (iii) The existing methods of disposal.

    (iv) Estimated annual cost of disposal.

c) Corporate management, policy or procedure for waste disposal.

d) Any published guidelines on disposal of toxic/hazardous materials.

After the mailing of the questionnaire, interviews will be arranged with companies who do not respond within a definite time, to clarify responses as necessary to obtain clear information, and perhaps to explain the questionnaire, its purpose, etc., and if necessary to reassure manufacturers concering the confidentiality of the information collected.

During this year, the main thrust will be to obtain maximum information, through the questionnaire and interviews, to establish a data base, and to work out more detailed procedures for inventory and approaches to the next stage. The data obtained will be checked through the Ministry of the Environment's computer for accuracy. Our findings will be presented for discussion at the next conference in this series.

TABLE I

PHARMACEUTICAL COMPANIES

Adria Laboratories of Canada
4500 Dixie Road
Mississauga, Ontario L4W 1V7

Alcon Canada Ltd.
6500 Kitimat Road
Mississauga, Ontario L5N 2B8

Allen Hanburys
1025 The Queensway
Toronto, Ontario M8Z 5S6

Ames Company
Division, Miles Laboratories Ltd.
77 Belfield Road
Rexdale, Ontario M9W 1G6

Anca Inc.
111 Consumers Drive
Whitby, Ontario L1N 4Z5

Astra Pharmaceuticals Canada Ltd.
1004 Middlegate Road
Mississauga, Ontario L4Y 1M4

Boehringer Ingelheim (Canada) Ltd.
977 Century Drive
Burlington, Ontario L7L 5J8

Bristol-Meyers Canada Inc.
431 Dundas Street East
Belleville, Ontario K8M 5C2

CIBA Pharmaceuticals
Division of CIBA-GEIGY Canada Ltd.
6860 Century Avenue
Mississauga, Ontario L5N 2W5

Connaught Laboratories Limited
1755 Steeles Avenue West
Willowdale, Ontario M2R 3T4

Coopervision Inc.
250 Consumers Road, Suite 1103
Willowdale, Ontario M2J 4V6

Dow Pharmaceuticals
Dow Chemical Canada Ltd.
380 Elgin Road East
Richmond Hill, Ontario L4C 5H2

Fisons Corporation Limited
80 Melford Drive
Scarborough, Ontario M1B 2G3

Glaxo Canada Limited
1025 The Queensway
Toronto, Ontario M8Z 5S6

ICI Pharma
16 Falconer Drive
Mississauga, Ontario L5N3M1

Johnson & Johnson Inc.
890 Eoodlawn Road West
Guelph, Ontario N1M 7L4

Lederle Products
Cyanamid Canada Inc.
2255 Sheppard Avenue East
Willowdale, Ontario M2J 4Y5

Eli Lilly Canada Inc.
3650 Danforth Avenue
Scarborough, Ontario M1N 2E8

McNeil Laboratories (Canada) Ltd.
600 Main Street West
Stouffville, Ontario L9H 1L0

Miles Pharmaceuticals
Division of Miles Laboratories Ltd.
77 Belfield Road
Rexdale, Ontario M9W 1G6

Norwich-Eaton
Division of Morton-Norwich Products Inc.
Paris, Ontario W3L 3T8

Novopharm Ltd.
1290 Ellesmere Road
Scarborough, Ontario M1P 2Y1

Organon Canada Ltd.
585 Coronation Drive
West Hill, Ontario M1E 4S2

Ortho Pharmaceutical (Canada) Ltd.
19 Green Belt Drive
Don Mills, Ontario M3C 1L9

TABLE 1

Parke-Davis Canada Inc.
2200 Eglinton Avenue E.
Scarborough, Ontario M1K 5C5

Pennwalt of Canada Ltd.
Pharmaceutical Division
393 Mildwest Road
Scarborough, Ontario M1P 3A6

The Purdue Frederick Company (Canada) Ltd.
123 Sunrise Avenue
Toronto, Ontario M4A 1A9

Riker Canada Inc.
P.O. Box 5757
London, Ontario N6A 4T1

A.H. Robins Canada Inc.
2393 Dunwin Drive
Mississauga, Ontario L5L 1T1

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Sterling Products
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Syntex Limited
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Wampole Limited
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Westwood Pharmaceuticals
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Wyeth Limited
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Pfizer Canada Ltd.
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Warner-Lambert Canada Inc.
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TABLE II

CLASSES OF PHARMACEUTICALS

1. Antihistamines
2. Antitussives and Expectorants
3. CNS Drugs including Sedatives, Anticonvulsants, Anaesthetics and Analgesics
4. Psychotherapeutics
5. Cardiovascular Agents
6. Corticosteroids
7. Hormones and synthetic substitutes, including Estrogens
8. Anti-infective agents including Antibiotics
9. Biologicals, including vaccines
10. Antineoplastics
11. Organic based Pharmaceuticals
12. Mineral Based Pharmaceuticals

REFUSE PYROLYSIS EMISSIONS TESTING

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Key words: Refuse, Municipal Solid Waste, Pyrolysis, Emission Rate, Incineration, Hazardous Contaminants, Hazard Assessment.

ABSTRACT

EFW Systems Incorporated has built and is currently evaluating the performance of a 1 tonne/h municipal solid waste (MSW) pyrolysis unit. The feed to the unit consists essentially of shredded MSW combustibles. Low energy gas product will be combusted and used both to sustain pyrolysis and to produce about 350 Kw of electricity.

The Ministry of Energy requested the Ontario Research Foundation to evaluate the performance of the pyrolysis unit, primarily by determining the composition of the gaseous product and by determinig the emission rates of contaminants in the product. Contaminants included in the evaluation were:

- particulate matter
- acid gases
- gases
- dioxins and furans
- PCBs, chlorobenzenes and chlorophenols
- polycyclic aromatic hydrocarbons
- trace metals

The purpose in measuring these emission rates was to identify any potential environmental hazards associated with generation and use of the pyrolyser gases. This included confirming the emission rates of the above contaminants with current environmental standards and developing contaminant emission factors.

1. INTRODUCTION

With increased difficulties in locating suitable landfill sites for municipal refuse disposal, alternative disposal methods are being developed and implemented. These methods can be classified as either biological or thermochemical conversion. The thermochemical conversion methods are the most highly developed and are usually accompanied by energy recovery in addition to greatly reducing the volume of the refuse. For example, complete combustion is often used to generate steam for industrial use whereas partial combustion is used to produce fuels or chemical feedstock. Complete combustion facilities were initially developed many years ago and are currently in widespread use. There are some full-scale partial combustion facilities in operation but most of these processes are still in the developmental stage.

Recently, air pollution has been recognized as a potentially serious problem with complete combustion facilities for municipal refuse. Numerous studies have identified particulate matter, acid gases, trace organics and trace metals as contaminants which may be emitted in significant amounts. However, with adequate combustion conditions and appropriate air pollution control devices, emission rates of these contaminants can generally be maintained within Ontario air emission standards and guidelines. Fewer studies have been carried out to investigate potential air pollution problems associated with partial combustion processes. One of these processes is pyrolysis and a study was sponsored by the Ontario Ministries of Energy and the Environment to determine the emissions of airborne contaminants during refuse pyrolysis.

2. PYROLYSIS PROCESS

Refuse pyrolysis to produce a gaseous fuel involves heating the refuse in the absence of air to a temperature of about 800°C. The gaseous product, containing hydrogen, carbon dioxide, carbon monoxide, methane and water vapour as the major components in varying amounts, has a heating value of about 20,000 MJ/kg on a dry basis. This gas, usually termed a medium energy gas, requires treatment to remove impurities such as particulate matter, gaseous impurities and condensible organics before it can be used as a fuel or for other purposes.

The pyrolysis system investigated in this study is a prototype unit, built and currently under development by EFW Systems Incorporated. This is a moving bed system with a nominal feed rate of 1 tonne per hour, although the feed rate during the study was about 545 kg/h of shredded refuse with inorganic components removed (refuse derived fuel, RDF) and containing about 10% moisture.

At present, indirect propane combustion is used to initiate pyrolysis of the RDF and the pyrolysis gases are flared to the atmosphere without further treatment. During commercial operation, a portion of the pyrolyser gases will be directly combusted to provide heat for pyrolysis initiation and the remainder will be combusted in an internal combustion engine to generate electricity.

Emission tests were carried out on the raw pyrolysis gases prior to flaring by the Ontario Research Foundation.

3. TESTING PROGRAM

On the basis of results from previous emission tests at refuse combustion facilities, the following groups of potential contaminants were included in the present study.

- particulate matter
- acid gases

- dioxins and furans
- PCB's, chlorobenzenes and chlorophenols
- polycyclic aromatic hydrocarbons
- trace metals

Of principal concern to the study were dioxins (polychlorinated dibenzo-p-dioxins) and furans (polychlorinated dibenzofurans). These compounds are extremely toxic and are probably always present in the flue gases from refuse combustion. Studies have shown that amounts can be significant compared with the Ontario provisional guidelines for these compounds in some incinerator emissions but with good combustion conditions (high temperatures, good mixing and adequate residence time) emission rates can be greatly reduced. The dioxins and furans are either present in the refuse or they are formed during combustion from percursor compounds such as PCB's, chlorobenzenes and chlorophenols. Some polycyclic aromatic hydrocarbons are extremely toxic and these compounds are also generally present in the flue gases from refuse incineration.

Particulate matter, acid gases, and trace metals are often emitted in significant amounts from refuse combustion but with appropriate air pollution control equipment concentrations can be reduced to levels generally below Ontario environmental standards and guidelines.

4. SAMPLING METHODS

Except for the gaseous components of the pyrolyser gases, sampling was carried out using modified EPA Method 5 sampling trains.

A single train was used for all the trace organic compounds. In a preliminary test, an ASME train was used in which the flue gas sample was passed successively through a probe, particulate filter, XAD-2 resin cartridge and impinger solutions. This test was unsuccessful, however, because organic compound quickly condensed in the resin cartridge and restricted the sample flow. Therefore, a different train was used in succeeding tests, which consisted of a probe, particulate filter, impinger solution and Florisil adsorbent cartridge. This train was developed by the Ontario Ministry of the Environment a few years ago and was shown to be effective for sampling trace chlorinated organics.

Particulate matter, acid gases and trace metals were sampled in a single train. The flue gas sample was passed successively through a probe, particulate filter, dilute sodium hydroxide impinger to collect acid gases and some metals (antimony, arsenic, selenium and tellurium), dilute nitric acid impingers to collect most metals, and an acidified potassium permanganate solution to collect mercury.

Gaseous concentrations were determined using either gas chromatography or continuous analyser techniques. The gases hydrogen, carbon monoxide, carbon dioxide, methane, nitrogen and C-2 hydrocarbons were analysed by gas chromatography using a Carbosieve SII column and a thermal conductivity detector. Tedlar bags (polyvinyl fluoride) were used to collect samples for this analysis. Continuous analysers were used for oxygen, sulfur dioxide and nitrogen oxides analyses.

5. SAMPLE TRAIN ANALYTICAL METHODS

All trace organic analyses of the flue gas samples were carried out using gas chromatography/mass spectrometry techniques and procedures described in the ASME draft method for chlorinated organics sampling.

Most trace metal analyses were carried out using d.c. plasma atomic emissions spectroscopy. Solutions were analysed directly, whereas particulate samples were digested with nitric acid and aqua regia before analysis. Silver was analysed by flame atomic absorption spectrophotometry and mercury by cold vapour atomic absorption spectrophotometry. Arsenic, antimony, selenium and tellurium were analysed by hydride generation atomic adsorption.

Acid gases were anlysed by ion chromatography. Cyanide was determined by a colorimetric method and ammonia was determined by reaction with Nesslar reagent.

6. RESULTS

The sampling program at the pyrolyser was completed fairly recently and many of the sample analyses, including all the trace organic analyses, were not available when this paper was prepared. Some preliminary results, however, are presented.

Gaseous component concentrations in the pyrolyser gases after drying (Table 1) indicate hydrogen predominates with lesser amounts of carbon monoxide, methane and carbon dioxide. Other identified minor components are present in insignificant amounts. Unidentified components are believed to be mainly residual moisture and hydrocarbons. On a dry basis and excluding minor components, the higher heating value of the gaseous product is 21,330 MJ/kg or 15,030 MJ/Nm^3.

Trace metal concentrations in the pyrolyser gases are shown in Table 2. Except for mercury, the predominant amount of each metal was associated with particulate material, and could be removed from the gases by a suitable particulate control device. To place the concentrations in perspective, they are compared with Ontario Environmental Protection Act Regulation 308, maximum allowable impingement concentrations in Table 3. Except for beryllium, which was not detected in any sample but had a relatively high detection limit. The most significant metals in the non-particulate phase are mercury, cadmium, manganese and nickel.

Similarly, acid gas and ammonia concentrations in the pyrolyser gases are compared with Regulation 308 concentrations in Table 4. The most significant of these components are hydrogen cyanide and ammonia.

Average gaseous contaminant concentrations in the pyrolyser gases were 1.50 g/Nm^3 hydrogen sulfide, 0.65 g/Nm^3 sulfur dioxide and 0.02 g/Nm^3 nitrogen oxides (as nitrogen dioxide).

Further evaluation of the pyrolyser emissions and performance will be made when all sample analyses are completed.

TABLE 1

Refuse Pyrolysis Emissions

Average Dry Gaseous Component Concentrations

Gas	Average Concentration %
Hydrogen	35.56
Methane	19.09
Carbon Monoxide	17.85
Carbon Dioxide	14.66
C2 - Hydrocarbons	1.42
Nitrogen	0.88
Ammonia	0.35
Oxygen	0.19
Hydrogen Sulfide	0.11
Hydrogen Cyanide	0.10
Sulphur Dioxide	0.03
Other*	9.76
Total:	100.0

*Including Residual Moisture, Hydrocarbons and Acid Gases.

TABLE 2

Refuse Pyrolysis Emissions

Trace Metal Concentrations

Metal	Test 1 mg/m^3	Test 2 mg/m^3	Test 3 mg/m^3	Average mg/m^3
Aluminum	203	37	9	83
Antimony	21	1.1	0.2	7.4
Arsenic	0.6	1.0	0.2	0.6
Barium	8.4	2.6	0.3	3.8
Beryllium	0.3	0.2	0.2	0.2 (ND)
Bismuth	6.1	10.3	2.3	6.2
Boron	74	8.3	6.2	30
Cadmium	2.8	3.5	0.8	2.4
Calcium	397	68	28	164
Chromium	1.3	2.1	0.8	1.4
Cobalt	1.1	5.4	0.6	2.4
Copper	11	4.4	1.0	5.5
Iron	81	8730	530	3100
Lead	42	27	10	26
Magnesium	32	10	4.1	15
Manganese	1.3	40	19	20
Mercury	3.2	0.5	2.7	2.1
Molybdenum	2.5	2.1	1.6	2.1
Nickel	5.2	2.8	0.8	2.9
Phosphorous	10	16	4.0	10
Selenium	0.2	0.1	0.1	0.1 (ND)
Silicon	70	69	50	63
Silver	0.3	0.2	0.2	0.2
Sodium	109	93	26	76
Tellurium	0.2	0.1	0.1	0.1 (ND)
Tin	3.7	1.6	1.2	2.2
Vanadium	1.2	0.8	0.6	0.9
Zinc	15	40	13	23

ND = None Detected.

TABLE 3

Refuse Pyrolysis Emissions

Comparison of Metal Concentrations with Regulation 308

Metal	Total Average Concentration mg/m^3	Non-Particulate Average Concentration mg/m^3	Maximum Regulation 308 Concentration µg/m^3	Total Concentration Ratio	Non-Particulate Concentration Ratio
Antimony	7.4	0.6	75	99	8
Arsenic	0.6	0.1	15	40	7
Beryllium	0.2 (ND)	0.06 (ND)	0.03	6700	2000
Boron	30	3.6	100	300	36
Cadmium	2.4	0.5	5.0	480	100
Chromium	1.4	0.3	5.0	280	60
Copper	5.5	0.4	100	55	4
Lead	26	0.5	10	2600	50
Manganese	20	8.2	100	200	82
Mercury	2.1	2.1	5.0	420	420
Nickel	2.9	0.4	5.0	580	80
Selenium	0.1 (ND)	0.06 (ND)	20	5	3
Silver	0.2	0.06	3.0	67	20
Tellurium	0.1 (ND)	0.04 (ND)	30	3	1
Tin	2.2	0.5	30	73	17
Vanadium	0.9	0.3	5.0	180	60
Zinc	23	0.9	100	230	9

ND = None Detected.

TABLE 4

Refuse Pyrolysis Emissions

Comparison of Inorganic Concentrations with Regulation 308

Compound	Average Concentration mg/m^3	Maximum Reg. 308 Concentration µg/m^3	Concentration Ratio
Hydrogen Fluoride	0.54	4.3	126
Hydrogen Chloride	8.2	100	82
Phosphoric Acid	2.7	100	27
Nitric Acid	4.1	100	41
Sulfuric Acid	202	100	202
Hydrogen Cyanide	1088	1150	946
Ammonia	2471	3600	686

APPROACHES TO MINIMIZING SOLVENT EFFECTS IN MUTAGENICITY ASSAYS

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Key words: Mutagenicity, Organic Solvent, Analytical Methods.

ABSTRACT

Testing of potentially hazardous chemicals usually requires that they be dissolved in a suitable solvent prior to administration. In many cases the chemicals are hydrophobic, necessitating the use of organic solvents. Unfortunately, in recent years it has become clear that many organic solvents interfere with or modify the response of an assay. Such solvent effects may include high solvent toxicity, the introduction of solvent derived mutagens or alteration of an assay response to known mutagens. In each case, the data obtained are equivocal and of questionable utility. Even the use of such popular solvents as DMSO has proven unsatisfactory in some assay systems.

Minimising solvent effects is emerging as a major problem in mutagenicity testing. Our approach to the problem has involved testing a variety of natural and artificial oils as potential solvents. Natural plant oils, e.g. corn, olive and sunflower, have low toxicity and suitable solubility characteristics; however, we have found that there remain problems with their use. These problems derive from the aging of such oils and their variable composition, in particular the variable amounts of minor constituents such as tocopherols which have been shown to interfere with the expression of mutagenicity in several assay systems. The use of pharmaceutical grades of plant oils does not eliminate the problems since pharmaceutical standards allow the inclusion of modest and variable amounts of the troublesome ingredients. Clearly, if natural oils are to be used internationally, more restrictive standards for their composition and use will be required. An alternative approach is the use of synthetic oils which include none of the presumed deleterious ingredients. In this case, the solvent composition can be adjusted to provide the best compromise between different chemical and physical characteristics. For example, the degree of saturation of triglyceride substituted fatty acids affects the viscosity, solvent capability and susceptibility to oxidation of triglycerides. We will demonstrate the use of such solvents in a widely used *in vivo* assay system.

APPROACHES TO MINIMIZING SOLVENT EFFECTS IN MUTAGENICITY TESTING

D.M. Logan, S. Chiu (York University), M.F. Salamone
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Biological testing of a chemical often requires that it be dissolved in an appropriate solvent. For many chemicals, water or saline is the obvious solvent. In biological systems the water or saline is thought to be innocuous and is not thought to affect the outcome of the assay. The study of hydrophobic substances, however, has introduced a new problem. Such substances must usually be dissolved in organic solvents for testing and it is becoming clear that the use of such solvents often does affect the outcome of the assay. This is of particular concern in the testing of potentially hazardous chemicals where a positive response may be disguised or lost and the danger unrecognized.

In this report we wish to outline the range of different solvent effects which have been reported and consider approaches to the reduction or elimination of such effects. To this end we have investigated the effect of certain solvents in two mammalian in vivo assays, the micronucleus and abnormal spermhead assays.

MATERIALS AND METHODS

MATERIALS:

The chemicals tested and their structural analogs were obtained from Eastman Kodak and Imperial Chemical Industries. The lipid solvents were obtained from Nu Chek Prep (Elysian Mn.) and Sigma Chemical Co. All other chemicals were obtained from standard suppliers and unless indicated otherwise were the highest purity available.

METHODS:

All mutagenicity studies were conducted with B6C3F1 hybrid mice purchased from Charles River of Canada. The micronucleus assay procedure used here followed that described by Salamone and Heddle (1983) and Heddle et al. (1984). The abnormal spermhead assay used here was that of Wyrobek et al. (1983).

RESULTS AND DISCUSSION

1. Types of solvent effects.

The use of organic solvents introduce several different types of problems and it is not possible at this time to predict which problem(s) may arise when using a particular solvent/assay system combination. The types of problems which have been encountered include the following; [summarized in table #1.]

(a) General Enzymatic Assays

Lipid metabolism studies often include the measurement of critical synthetic degradative enzymes. *In vitro* assays of such enzymes usually require that the substrate be dissolved in a suitable organic phase and mixed with an aqueous solution of the enzyme. After an appropriate incubation period, the product may be isolated and measured using additional organic solvents. In such systems, for example the enzymes of cholesterol synthesis, it is difficult if not impossible to calculate even simple kinetic characteristics such as Km and Vmax and activity measurements are often suspect. Similarly, in mutagenicity tests requiring S9 activation, a negative result will always be equivocal since enzymatic activation, may be absent and therefore the active agent (ie the mutagen) may not be formed.

(b) Mutagenicity Assays

A variety of solvent effects can be anticipated with different organic solvents in various assay systems.

(1) Solvent derived active reactants.

It is possible that the solvent of choice is itself a genotoxin and, thus, will interact with the test tissue to produce misleading results. For example, croton oil produces artifactual results in some carcinogenesis assays. Fortunately, most of this class of solvents are extremely toxic to living tissue and therefore are seldom used in biological assays.

(2) Solvent induced reactants derived from the test substance.

In some cases the interaction of solvent and test substance produce artifactual mutagens which emerge only with a particular solvent/test substance combination. For example, Nestman *et al* (1978) showed that trichloroacetic acid dissolved in DMSO produces short lived but mutagenic intermediate products. A similar stimulatory effect in dimethylsulfoxide (DMSO) solutions of p-phenylenediamine was observed by Burnett *et al*. (1982).

(3) Solvent dependant decreases in assay response

In some cases the solvent used may decrease or eliminate the positive assay response to a proven or suspected mutagen. For example, Yahagi *et al*. (1977) demonstrated that certain nitrosamines dissolved in DMSO lose their mutagenic activity in the Salmonella assay system and Nestman *et al*.(1985) reported that hexachloroacetone alone is mutagenic but loses this mutagenicity when dissolved in acetone. Less dramatic effects, ie. a diminution but not the elimination of a response have also been reported. Raj and Katz (1984) reported that minor constituents of corn oil solvents inhibit DMBA- induced chromosomal breaks *in vivo* and Nestman *et al*.(1985) reported that trichloroacetone is substantially less mutagenic in the Ames assay when dissolved in acetone rather than DMSO.

(4) Solvent dependant increases in assay response (sensitization)

In contrast to the case above, in some experiments the use of a particular solvent with a known mutagen produces a higher response than expected. This sensitization is a function of the mutagen/solvent combination rather than the solvent activity alone. In such cases a verdict of sensitization must always be cautious since the control solvent may in fact reduce the mutagen s activity. One is left then with a conundrum; does one mutagen/solvent pair show sensitization or is the control solvent/mutagen an example of decreased response. Such a decision can probably only be made when several control solvents have been tested. An example of what appears to be sensitization was reported by Arimoto *et al* (1982). In this case acetonitrile enhances the response of an Ames assay to Trp-P-1 and Trp-P-2 by an order of magnitude.

(5) Solvent induced kinetic changes

In certain assay systems, including the micronucleus assay system which we use, the product is produced maximally at a particular assay time. Interference with the kinetics of such a system may produce erroneously low assay values. For example, the micronucleus assay, which involves the complex reactions of erythropoeisis, usually involves sample times of 24, 48, and 72 hours after a treatment with a peak response usually in the middle of this range. A solvent which slowed absorption, transport or utilization of a test substance so that the assay peak occurred after 120 hours might produce an assessment of reduced or negligible hazard.

(6) Solvent interactions with S9 preparations

In certain assay systems the test chemical must be activated by incubation with an "S9" preparation. Recent reports indicate that certain solvents affect the activity of S9 preparations and hence the results of the final assay. For example, Mori *et al* (1985) reports that certain organic solvents inhibit the mutagenicity of N-nitrosodialkylamines in the Ames test. In this case, the solvent is not a desmutagen or antimutagen but rather produces its effect by interference with metabolic activation.

TABLE #1 SOLVENT EFFECTS

Types of solvent effect	Result
(a) General	
1 Enzyme assays with hydrophobic substrate.	Inaccurate kinetic constants
(b) Mutagenicity testing	
1 Solvent derivatives active in assay.	False positive assessment
2 Test substance derivatives active in assay.	False positive assessment
3 Decreased assay response.	Reduced or negative hazard assessment
4 Heightened assay response.	Excessive (possibly) hazard assessment
5 Altered assay kinetics.	Reduced hazard assessment
6 Solvent interacts with S9	Reduced hazard assessment

2. Approaches to Minimizing Solvent Effects.

An obvious approach to minimizing solvent effects is the use of alternative solvents. Many common organic solvents such as benzene, acetone, heptane, and methylene chloride are unsuitable because of their toxicity. This has led to the use of other solvents. For several years, one of the most widely used has been DMSO. It is only moderately toxic and offers a suitable solubility for many test chemicals. Recently however, an increasing number of difficulties in the use of DMSO have been reported, some of which have been outlined above. These problems have prompted a number of laboratories, ours included, to examine other potential solvents.

One group of potential solvents is plant oils such as corn, olive, and sunflower. Those oils are readily available, inexpensive, have low toxicity, and offer suitable solubility. Unfortunately, crude or only partially refined oils have two problems which will affect their use. However, both problems can be, at least partially, solved. The two problems which are interrelated are variability of composition and the inclusion of minor proportions of interfering substances such as antioxidants. Plant oils are essentially mixtures of triglycerides plus modest amounts of several minor constituents such as tocopherols and sterols. The specific triglycerides (ie. what fatty acids are substituted) in a particular batch of oil depends on many factors, such as the genetic composition of the plant and growth conditions (ie. soil, humidity, sunshine etc.). As a result, oils from the same species of plant prepared from different strains or at different times using the same strain will have composition differences. These differences will be in the proportions of particular substituted fatty acids and in the amounts of minor constituents. Fatty acid variability leads to variable life times, since oxidation rate depends on the degree of fatty acid unsaturation, and different physical characteristics such as viscosity. Of probably greater importance however will be the differing amounts of minor constituents such as tocopherols. Since the latter have been implicated in some solvent effects (Raj and Katz 1984), changes in their concentrations may produce dramatic effects. Several approaches to handling these problems exist.

An obvious first step would be purification of the oil. Unfortunately, current refinement standards are inadequate. For ezample, current pharmaceutical requirements allow the inclusion of pharmaceutical corn oil of non saponifiable material in concentrations adequate to significantly reduce an anticipated response.

An alternate approach is the use of pure triglyceride solutions. Although more costly, this approach eliminates both seasonal and crop variability and the presence of minor constituents. We have tested triolein, tricaprylin and tricaproin in the micronucleus and abnormal spermhead assays. Data on these and other solvents will be included in our final presentation.

CONCLUSION

Mutagenicity testing will, of course, continue to require the use of solvents. Unfortunately, no single solvent is ideal. Compared to other organic solvents, plant oils offer several advantages including low toxicity, and cost, suitable solubility properties and ready availability. Their major problems are variable composition and the presence or absence of minor components. The implications of these problems for mutagenicity testing must be assessed. In a single lab using oil from a single lot, data comparison should be satisfactory. Interlaboratory comparisons of data obtained using different oils will, however, be uncertain. This uncertainty could be minimized by the adoption of certain agreed upon criteria. First, in all cases the highest purity oil available should be used. For this purpose none of the pharmaceutical standards are adequate and should, for testing purposes, be replaced by a standard developed by or in conjunction with one of the international toxicological or mutagen testing organisations. We expect that such a standard would exclude trace antioxidants and other contaminents whose effects may vastly outweigh their proportions. In the current absence of such a standard it is essential that any oil stock be monitored on a regular basis to assess oxidation or breakdown and that when some low level of change has been reached, the oil be discarded. Second, there should be some international effort to decide upon a small number of common oils which would form the focus for future study. Within such a list the specific plant strains from which the oil is derived should be specified.

An alternative approach is the use of completely defined (synthetic) oils. These are mixtures of triglycerides selected to provide appropriate physical characteristics while avoiding the variability of natural oils and minimizing the possibility of trace contaminants. While significantly more expensive than natural oils, they are free of the latter's variability and contaminant problems. If further study reinforces their desirability then, as above, international collaboration should be encouraged to develop international standards.

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LEACHING STUDIES OF PCDD AND PCDF FROM MUNICIPAL INCINERATOR FLYASH

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Key words: Leachate, Dioxins, Furans, Flyash, Water Quality, Municipal Incinerators, Analysis.

ABSTRACT

This study concerns the possibility of polychlorodibenzo-p-dioxins (PCDD) and polychlorodibenzofurans (PCDF) entering the environment through the leaching of municipal incinerator flyash into water. The study also takes into account the effect of the pH of water on the extent of leaching.

Several methods for simulating the actual conditions by which flyash comes into contact with water were investigated. A Soxhlet extraction of flyash with water was finally chosen for this leaching study because of its simulation of the circulation of water in nature and because of its high extraction efficiency. Following the extraction, a simple benzene-water partitioning step was used to transfer the organic compounds in the water extracts into organic solvent for a subsequent GC and GC/MS analysis. Good recovery of PCDD at the 2 ppt level was obtained using benzene partitioning.

The analytical results for water extracts at pH levels of 4, 7, and 10 show clearly that PCDD and PCDF enter water through leaching. These compounds were found in water at the 1 to 400 ppt level. Because of these low concentration levels, the reproducibility and accuracy of quantitative results were poor.

The study was extended to identification of other organic compounds that were also leached from the flyash into the water extracts. Identification of these organic compounds was accomplished using the techniques of GC/FID, GC/EIMS, GC/PICIMS and GC/NICIMS. These compounds were present at higher concentrations than the PCDD and PCDF and many were chlorinated and toxic. At pH 4, a total of 71 compounds were found; at pH 7, 64 were found, and at pH 10, 56.

ABSTRACT

This study concerns the possibility of polychlorodibenzo-p-dioxins (PCDD) and polychlorodibenzofurans (PCDF) entering the environment through the leaching of municipal incinerator flyash into water. A Soxhlet extraction of flyash with water was finally chosen for this leaching study because of its simulation of the circulation of water in nature and because of its high extraction efficiency. Following the extraction, a simple benzene-water partitioning step was used to transfer the organic compounds in the water extracts into organic solvent for a subsequent GC and GC/MS analysis. Good recovery of PCDD at the 2 ppt level was obtained using benzene partitioning.

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The study was extended to identification of other organic compounds leached from the flyash into the water extracts. Identification of these organic compounds was accomplished using the techniques of GC/FID, GC/EIMS, GC/PICIMS and GC/NICIMS. These compounds were present at higher concentrations than the PCDD and PCDF and many were chlorinated and toxic.

INTRODUCTION

In many large cities throughout the world, municipal waste is disposed of by incineration in large plants. The amount of urban waste disposed of in this manner worldwide is staggering. Canada, for example, disposes of an estimated 2.0 million tons of waste by incineration annually. A fine particulate known as flyash is formed in the combustion zone in the incinerator. This product is precipitated electrostatically and then requires disposal. Approximately 35,000 tons of flyash are produced for each million tons of waste incinerated. It is therefore important to study the environmental and health effects of flyash.

The composition of flyash has been studied extensively. It is composed of 70-95% inorganic matter such as SiO_2, Al_2O_3, Na_2O, and Fe_2O_3 (1). Adsorbed on the inorganic matter are many organic compounds in the ppm to ppb range. More than 600 organic compounds are known to be present, 200 of which have been identified in this complex organic mixture. These compounds include hydrocarbons, phthalates, polycyclic aromatic hydrocarbons (PAH) and polychlorinated organic compounds (2).

Many of the organic compounds identified in flyash are known to be toxic. Some PAH found in flyash are toxic, carcinogenic and mutagenic (3). Of widespread concern are two classes of compounds known as polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF). Some PCDD isomers, particularly 2,3,7,8-tetrachlorodibenzo-p-dioxin (2378-TCDD) are extremely toxic (4). Recently, public concern about the toxicity of the PCDF has been growing. Because these hazardous compounds are found in municipal flyash, regardless of the design of the incinerator or the type of garbage burned, the effect of flyash residue in the environment is an important concern.

One way in which flyash enters the environment is through stack emission. Approximately 1-2% of the flyash produced is not captured by the electrostatic precipitators and escapes to the atmosphere with the stack gases (4). This visible, airborne emission is generally the aspect of flyash pollution found most objectionable by urban centres.

Most of the flyash, however, is trapped by the precipitators and has to be disposed of in some manner. Flyash is most often dumped or buried in landfill sites. This method seems the most economical and practical way to dispose of flyash. However, much of the flyash dumped or buried in a landfill site is constantly exposed to ground water that includes rain-water and possibly wastewater as well. It is important to know whether PCDD and PCDF or other organic pollutants in the flyash could be removed by water leaching and contaminate the environment. Little if any investigation has been done regarding this possibility.

The major purpose of this study was to investigate the possibility of PCDD and PCDF entering the environment through the leaching of flyash with water. The behaviour of other organic compounds in flyash was also investigated. The most important step in the study was to design an experiment that would resemble actual conditions in which flyash comes into contact with water. Several difficulties were foreseen in the design of the experiment. First, water is not a good solvent for organic compounds. Therefore, assuming that organic compounds would indeed leach from the flyash, a large volume of water would be needed to accumulate enough organic material to reach the detection limit of the analytical method used. Second, the strong tendency for PCDD and PCDF to adsorb onto glass necessitates that the aqueous organic mixture be exposed to a minimal surface area of glass.

The general method chosen to represent the leaching process was extraction of organic compounds from flyash with water. A Soxhlet extraction of flyash with water was finally chosen for this study. The basic process of a Soxhlet extraction is very similar to the natural circulation of water - vapourization, condensation, and precipitation. The Soxhlet extraction, therefore, seemed most representative of the actual leaching process in disposal sites. In addition, fresh solvent is passed through the flyash during each cycle, thereby achieving a high extraction efficiency. An exhaustive extraction, it was assumed, would give us an idea of the extent of leaching in the most serious case, where the flyash is in a totally aqueous environment.

Because of exposure to different water sources which include industrial waste-water, flyash in landfill could be exposed to water with different pH conditions. The three pH values used in this study were 4, 7 and 10. Those three pH values cover the normal pH range of waste water discharged from most industries. The organic compounds in the water extracts obtained from the three different conditions were subjected to an extensive analysis. Five techniques were used in the course of analysis of PCDD, PCDF and other organic compounds in the water extracts of flyash. They included gas chromatography with flame ionization detection (GC/FID) and with electron capture detection (GC/ECD), gas chromatography/mass spectrometry with electron impact ionization (GC/EIMS), with positive ion chemical ionization (GC/PICIMS), and with negative ion chemical ionization (GC/NICIMS). PCDD, PCDF and a number of other organic compounds were found in the water extracts of flyash by these analytical methods.

EXPERIMENTAL

Solvents, Standards, and Flyash Sample

All solvents used were distilled in glass, UV grade, supplied by Caledon Laboratories (Georgetown, Ontario, Canada), with the exception of the water, which was deionized tap water. The standards of 1,2,3,4-tetrachlorodibenzo-p-dioxin (1234-TCDD), 1,2,3,4,7,8-hexachlorodibenzo-p-dioxin (123478-H_6CDD), 1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin (1234678-H_7CDD) and octachlorodibenzo-p-dioxin (OCDD) were all purchased from Ultra Scientific (Hope, RI, USA). The standard of 1,2,3,4,7-pentachlorodibenzo-p-dioxin (12347-P_5CDD) was obtained from Cambridge Isotope Laboratories Inc. (Woburn, MA). The formic acid, sulfuric acid and sodium hydroxide were purchased from J.T. Baker Chemical Co. (Phillipsburg, NJ, USA) and the 2-methoxyethylamine was purchased from Aldrich Chemical Co. (Milwaukee, Wis., USA). All glassware was carefully cleaned, and finally rinsed three times with benzene and 3 times with dichloromethane, immediately before use.

The flyash sample was collected in kilogram amounts from the electrostatic precipitator of a municipal incinerator in Toronto, Ontario, Canada. The sample was stored at room temperature, away from ultraviolet and visible light.

Soxhlet Extraction of Flyash with Water

Approximately 300 mL benzene were run through the Soxhlet apparatus for 1 hr prior to use, followed by 300 mL water run for several hrs to ensure the removal of contaminants. A 50 g sample of flyash was placed in a coarse porosity fritted glass extraction thimble and smoothly extracted for 48 hr with 500 mL water in a Soxhlet apparatus. After the extraction, the Soxhlet apparatus was dismantled, and the Soxhlet extractor and the outside of the thimble were rinsed with 50 mL water to remove all traces of flyash. This water was added to that already in the round bottom flask. The same glass surfaces were then rinsed with a 50 mL volume of benzene, which was placed in a separatory funnel. The thimble was emptied and all visible traces of flyash were removed by rinsing the thimble under the deionized water tap. The thimble was then used to filter all the water previously collected, which was then transferred to the separatory funnel. Several water rinses of the round bottom flask were also filtered through the thimble into the separatory funnel. The thimble was again rinsed under the tap to remove any particulate matter, then 25 mL benzene were forced through the thimble by applying positive pressure at the top of the thimble with a rubber bulb. The round bottom flask was rinsed several times with a total of 25 mL benzene, which was added to the separatory funnel.

For the extraction at pH 7, deionized water was used and no extra chemical was employed.

For the extraction at pH 4, the water was acidified using formic acid prior to extraction.

For the extraction at pH 10, the water was made basic with 2-methoxyethylamine prior to extraction.

A magnetic Teflon stir bar was used in conjunction with a hot plate/stirrer to mix the water constantly. The heating mantle was placed on top of the hot plate/stirrer. The vortex of the water was kept close to the bottom of the flask to ensure good heat transfer.

The extraction was performed in duplicate at each pH condition, and an extraction blank which used the same method but omitted the flyash was also run at each pH condition.

Benzene-Water Partitioning

After the Soxhlet extraction at pH 7, enough benzene was added to the separatory funnel to bring the total volume of benzene to 150 mL, and this volume was used as the first of three 150 mL aliquots of benzene used for solvent extraction. The three aliquots of benzene extract were combined and the volume was reduced to approximately 15 mL by rotary evaporation under aspirator vacuum. The extract was then transferred to a cone bottom flask with a Pasteur pipet, followed by several benzene rinses of the round bottom flask, and the volume was further reduced to approximately 5 mL in the same manner. The top phase in the cone (the benzene phase) along with several benzene rinses were transferred by Pasteur pipet to a small cone bottom flask, taking care not to transfer any of the aqueous phase. The volume in the flask was reduced to approximately 1 mL using rotary evaporation under aspirator vacuum and then transferred with several benzene rinses to a calibrated 1 mL reacti-vial. The volume was reduced to 50 µL under a gentle stream of high purity nitrogen. The vial was sealed with a screw cap fitted with a Teflon seal, and stored at -15°C.

The pH 4 water extract was neutralized with sodium hydroxide prior to solvent partitioning.

The pH 10 water extract was neutralized with sulfuric acid prior to solvent partitioning.

The recovery studies of benzene-water partitioning were performed on a PCDD standard mixture containing 1234-TCDD; 12347-PCDD; 123478-H_6CDD, and 1234678-H_7CDD. The standard solution was diluted to various concentrations and was then used for the study of recovery at different concentration levels. When the detection limit of GC/ECD was reached the concentration of standard solution was approximately 50 ppb in benzene. A 10 µL volume of this solution was used to spike a 250 mL volume of water to give a final concentration for each dioxin component of approximately 2 ppt. The flask was shaken and allowed to sit for 30 min, then the benzene-water partitioning procedure was used as described above with exception of the use of 2 X 50 mL aliquots of benzene. A 25 mL volume of benzene was used to finally rinse the separatory funnel, then the total volume of benzene was reduced to dryness in the manner described above and diluted to 20 µL with benzene for the analysis by GC/ECD.

Once the detection limit of GC/ECD was reached, the recovery study was performed in duplicate.

Gas Chromatographic Analysis

GC analyses were carried out on a Hewlett-Packard HP 5880A gas chromatograph equipped with a flame ionization detector (FID) and an electron capture detector (ECD). A cool on-column injector and a 30 m x 0.32 mm I.D. Durabond DB5 fused silica capillary column (J & W Scientific, Rancho Cardova, CA, U.S.A.) were used for both the FID and ECD analyses. A microcomputer data system and cartridge tape allows storage of chromatographic information for further calculations. The GC conditions for both methods of detection were as follows: injection port temperature at less than 50°C; column temperature programmed from 80°C to 300°C at 5°C/min with initial 1 min and final 10 min isothermal periods; detector temperature 350°C and helium carrier gas flow rate 3 mL/min at room temperature.

Gas Chromatographic/Mass Spectrometric Analysis

GC/MS analyses were performed using a Hewlett-Packard HP 5987A GC/MS system with an HP 1000 data system and an HP 7914 Winchester disk drive.

For the electron ionization (EI) mode, an ionization voltage of 70 eV and a source temperature of 250°C were used. A direct interface kept at 300°C linked the HP 5880A to the mass spectrometer. Both linear scanning (50-500 amu) and selected ion monitoring (SIM) were used. Using SIM, it is possible to monitor up to 5 different groups of ions with up to 20 selected ions in each group. The system provided for data acquisition and storage allows the reconstruction of chromatograms at any mass in the scan range. During or after a run, the mass spectrum of any peak on the total ion chromatogram (TIC) trace may be obtained. To help identify compounds by their mass spectra there is a library search system which incorporates a probability based matching system (PBM) based on 70,000 reference spectra as well as a self-training interpretive retrieval system (STIRS).

The column used was a 30 m x 0.25 mm Durabond DB-5 fused silica capillary column. The GC conditions were the same as those used for the GC analysis.

The GC/MS was also operated in the chemical ionization (CI) mode. The reagent gas for CI was methane. The source temperature for positive ion chemical ionization (PICI) was 200°C and it was 100°C for negative ion chemical ionization (NICI).

RESULTS AND DISCUSSION

Soxhlet Extraction and Benzene-Water Partitioning

Most organic compounds which have been found in flyash exhibit very low solubilities in water. To remove a sufficient amount of organic compounds from flyash for the following analysis, a large amount of water is needed and highly efficient contact between water and flyash must be achieved. In practice, those requirements are difficult to fulfill using mechanical and ultrasonic agitation methods. Few organic compounds were found in the water samples treated by these two methods. PCDD and PCDF were not detected in these samples (5). In addition, the analytical results obtained from these two methods were irreproducible due to the manual operation. To provide a more exhaustive and reproducible extraction a Soxhlet extraction was finally used for the leaching study. Figure 1 is a schematic diagram showing the sample preparation procedure and the subsequent analysis of PCDD, PCDF, and other organic compounds in water.

In nature, there is a constant circulation of water - vapourization, condensation and precipitation. This circulation is similiar to the basic process of a Soxhlet extractor. Therefore, the Soxhlet extraction of flyash with water is a good simulation of leaching flyash with water in nature. In a thimble, flyash always contacts fresh water which is condensed. By recycling, a significant amount of organic compounds can be gradually removed from the flyash, even those with low solubilities in water. A relatively small amount of water provides a highly efficient extraction of organic compounds in a Soxhlet extraction procedure. Eventually, organic compounds removed from flyash can be accumulated in the water extract to a detectable quantity. This also reflects the phenomenon of nature, in which the organic compounds are gradually leached away by water from the flyash.

In contrast to the low solubility of organic compounds in water, many trace organic compounds have a strong tendency to adsorb on a glass surface. When large glass surface areas are involved in a water sample preparation, the loss of organic compounds due to such adsorption could be significant. This loss usually leads to low recovery and poor reproducibility. Furthermore, some trace organic compounds may be below the limit of detection owing to the adsorption. It has been found in this study that trace PCDD and PCDF adsorb strongly on glass surfaces. This adsorption problem has been effectively minimized using a Soxhlet extractor because no large volume glassware apparatus are required. In addition, all glassware surfaces which made contact with the water extract were carefully rinsed with benzene, and then these benzene aliquots were collected for organic compound analysis. However, during the entire sample preparation, direct contact of flyash with benzene was prevented to ensure that the organic compounds found were removed from the flyash solely by water.

To expose the organic compounds in the water extract to a minimal glass surface area, a simple benzene-water partitioning procedure was used to transfer the organic compounds from the water extracts into benzene for the subsequent analysis. This method minimizes the loss of trace organic compounds that usually occurs during a complicated procedure, and also provides a high transfer efficiency due to the greater solubility of most organic compounds in benzene compared to water.

Dioxins Found in Water Extracts

A total of 14 Soxhlet extractions of flyash were carried out at pH 4, 7, and 10. Those 14 extracts were analyzed for PCDD and PCDF after benzene-water partitioning. The analytical techniques used included GC/ECD, GC/EIMS, GC/NICIMS, and GC/PICIMS. The results of PCDD detection are summarized in Table I. In these 14 water extracts, PCDD were detected in 8 samples by GC/ECD, and were more positively identified in 3 samples by GC/EIMS and GC/NICIMS.

Among the analytical methods used, GC/ECD analysis provided the highest sensitivity, in the sub-picogram range for PCDD and PCDF. However, because of the presence of interfering compounds in the water extract, TCDD and P_5CDD could not be positively identified on the GC/ECD chromatograms for some samples. There were less interfering peaks in the elution region of H_6CDD , H_7CDD, and OCDD on the GC/ECD chromatograms.Therefore, a typical pattern of H_6CDD, H_7CDD and OCDD, which was usually observed in a benzene-extract of flyash, could be easily recognized on a GC/ECD chromatogram of the extract sample containing PCDD. Figure 2 shows a typical GC/ECD chromatogram of the water extraction sample containing PCDD. A corresponding GC/ECD chromatogram of an extraction blank is also shown in Figure 2. No PCDD impurities were found in this blank. Finding dioxins by GC/ECD in Table 1 refers to detection of at least one of H_6CDD, H_7CDD and OCDD. For most samples more than one of the PCDD were identified by GC/ECD.

The presence of PCDD and PCDF were further confirmed by GC/EIMS/SIM and/or GC/NICIMS/SIM in three water extracts. Three criteria, i.e., two characteristic ions of each PCDD and PCDF congener, proper isotopic ion ratio, and proper retention time, were used for a positive identification of PCDD and PCDF. Figure 3 illustrates the GC/MS/SIM data of a water extract of flyash, showing evidence that PCDD and PCDF are present in water extraction samples. No PCDD or PCDF were found in the water blank analyzed by GC/MS/SIM.

A large variation exists in the concentrations of PCDD and PCDF found among these 14 extraction samples. This is most likely caused by the instability of trace amounts of PCDD and PCDF in water, and also by the problems encountered in an analysis at the ppt level. The differences among flyash samples from batch to batch could be another reason for the deviation. Therefore, exact quantification of PCDD and PCDF in the water extracts was not attempted in this study. Based on the limited results obtained, the concentration of PCDD leached into water is estimated to be in the 1 to 400 ppt range.

The recovery of PCDD using reference standards in the benzene-water partitioning procedure was investigated. The concentration level of PCDD standards in water was progressively lowered to the detection limit of GC/ECD. Due to interferences, this recovery study was limited to H_6CDD, H_7CDD, and OCDD standards. The recovery data given in Table II shows a good recovery of PCDD at the 2 ppt level.

Based on the results obtained both from the analysis of PCDD in water extracts and study of PCDD recovery, two conclusions can be reached. First, PCDD and PCDF can be leached from flyash by water at pH 4, 7, and 10. It is slightly easier to extract PCDD and PCDF into water at pH 7. Second, the precise quantity of PCDD and PCDF leached by water from flyash is difficult to determine because the levels of PCDD and PCDF are very low, and at such low levels, their tendency to adsorb onto glassware can present a problem for a reproducible quantification.

Identification of Organic Compounds in Water Extracts

In this study many organic compounds have been found in the water extracts. Five analytical techniques were used for such analysis. They included GC/FID, GC/ECD, GC/EIMS, GC/PICIMS and GC/NICIMS. The identification of most compounds was based on the data obtained from the three GC/MS analyses. The data of GC/FID and GC/ECD were used to facilitate the identification for some compounds. Utilizing the information of five analytical techniques, many compounds have been identified in the water extracts obtained at the different pH ranges studied. Table III lists the organic compounds which were identified or tentatively identified in the water extracts.

A combination of GC/EIMS, GC/PICIMS, and GC/NICIMS analyses provided a wealth of information for compound identification. Three total ion chromatograms (TIC) obtained from these three GC/MS methods of analyses for one water extract of flyash are illustrated in Figure 4. Although the same chromatographic conditions were used, these three total ion chromatogram (TIC) traces have different appearances. Some components that show no peaks on the GC/EIMS traces have good mass spectra using GC/NICIMS. The mass spectra obtained from the three GC/MS methods of analysis for a compound are complementary, facilitating compound identification. Such an example is given in Figure 5. Based on the EI mass spectrum (a), the most probable molecular weight of the unknown compound could be 254 or 177. However, a MW of 254 can be positively confirmed using the PICI mass spectrum (b) and NICI mass spectrum (c). The retention index obtained from GC/FID and GC/EIMS analyses indicates the unknown could be phenylphenanthrene or phenylanthracene. The spectra of NICIMS most likely rejects the possibility of the unknown compound being phenylphenanthrene because phenanthrene exhibits no response to NICIMS (6). Therefore, this unknown compound is tentatively identified as phenylanthracene.

Three Soxhlet extractions of water blanks were performed at the corresponding pH conditions. The few organic impurities found in these water extraction blanks were not incorporated in the list of compounds identified in the flyash sample extracts.

ACKNOWLEDGEMENTS

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TABLE I Number of Water Extraction Samples in Which PCDD Were Found.

pH	number of extracts	number of samples in which PCDD were detected		
		GC/ECD	GC/EIMS	GC/NICIMS
4	5	2	1	1
7	7	5	2	2
10	2	1	ND	ND

note: ND - non-detectable at the instrument detection limit

TABLE II Recovery of PCDD Standards in Benzene-Water Partitioning

compound	recovery (%)
OCDD	80
H_7CDD	61
H_6CDD	98

TABLE III Compounds Found in Water Extract

no.	compound	MW
1	dimethyl phenol	122
2	dichloropropenamide	139
3	3,4-dimethyl-3-hexen-2-one	126
4	octene alcohol	128
5	ethyl benzene	106
6	methoxy methyl benzonitrile	142
7	dichloro butadiene	132
8	octene ketone	126
9	tetrachloro pentene	206
10	bromobutanol	152
11	hydroxy biphenyl or its isomer	170
12	trichlorophenol	196
13	trichlorophenol	196
14	methyl biphenylamine	183
15	phthalate	bp 149
16	hydroxy methyl benzaldehyde	152
17	C_5-phenol	164
18	ethenyl tetrachlorobenzene	240
19	diphenylmethane/methyl biphenyl	168
20	2-ethyl biphenyl	182
21	trichlorocresol	240
22	ethenyl tetrachloro benzene	240
23	ui phthalate	bp 149
24	trichlorocresol	210
25	acenaphthene	154
26	N-ethylnaphthaleneamine	171
27	dimethoxy benzaldehyde	166
28	dimethyl phthalate	194
29	pentachloro benzene	248

Table III (continued)

no.	compound	MW
30	tetrachlorophenyl	164
31	tetrachlorophenol	230
32	amino-dimethylindan	161
33	diethyl phthalate	222
34	dichloroethenyl methyl benzene or its isomer	186
35	dichlorobenzamide	189
36	dichlorobenzamide	189
37	methyl benzenedicarboxylic acid	180
38	dimethyl biphenyl	182
39	dichlorobenzamide	189
40	dimethyl trichloro biphenyl	284
41	pentachlorophenol	264
42	ui trichloro N-compound[d]	223
43	ui trichloro N-compound	223
44	caffeine	194
45	methyl phenyl indole	207
46	ui trichloro N-compound	223
47	phenyl-9H-fluorene	242
48	ui trichloro N-compound	257
49	dimethoxy phenanthrene	238
50	ui pentachloro N-compound	291
51	ui pentachloro N-compound	291
52	diphenyl pyridine	231
53	9-phenyl phenanthrene	254
54	phenyl naphth[2,3-6]aze-2[H]one	245
55	trimethyl-diphenyl pyridinone	289
56	dioctyl phthalate	310
57	pentachlorochrysene	404

Table III (continued)

no.	compound	scan number	MW
	aliphatic hydrocarbons		
58	$C_{15}H_{32}$		212
59	$C_{16}H_{34}$		226
60	$C_{17}H_{36}$		240
61	$C_{18}H_{38}$		254
62	$C_{19}H_{40}$		268
63	$C_{20}H_{42}$		282
64	$C_{21}H_{44}$		296
65	$C_{22}H_{46}$		310
66	$C_{23}H_{48}$		224
67	$C_{24}H_{50}$		338
68	$C_{25}H_{52}$		342
69	$C_{26}H_{54}$		366
70	$C_{27}H_{56}$		380
71	$C_{28}H_{58}$		394
72	$C_{29}H_{60}$		408
73	$C_{30}H_{62}$		422
74	$C_{31}H_{64}$		436
75	$C_{32}H_{66}$		450
76	$C_{33}H_{68}$		464
77	$C_{34}H_{70}$		478
78	$C_{35}H_{72}$		492
79	$C_{36}H_{74}$		506

Note: ui - unidentified.
bp - base peak on mass spectrum.

FIGURE CAPTIONS

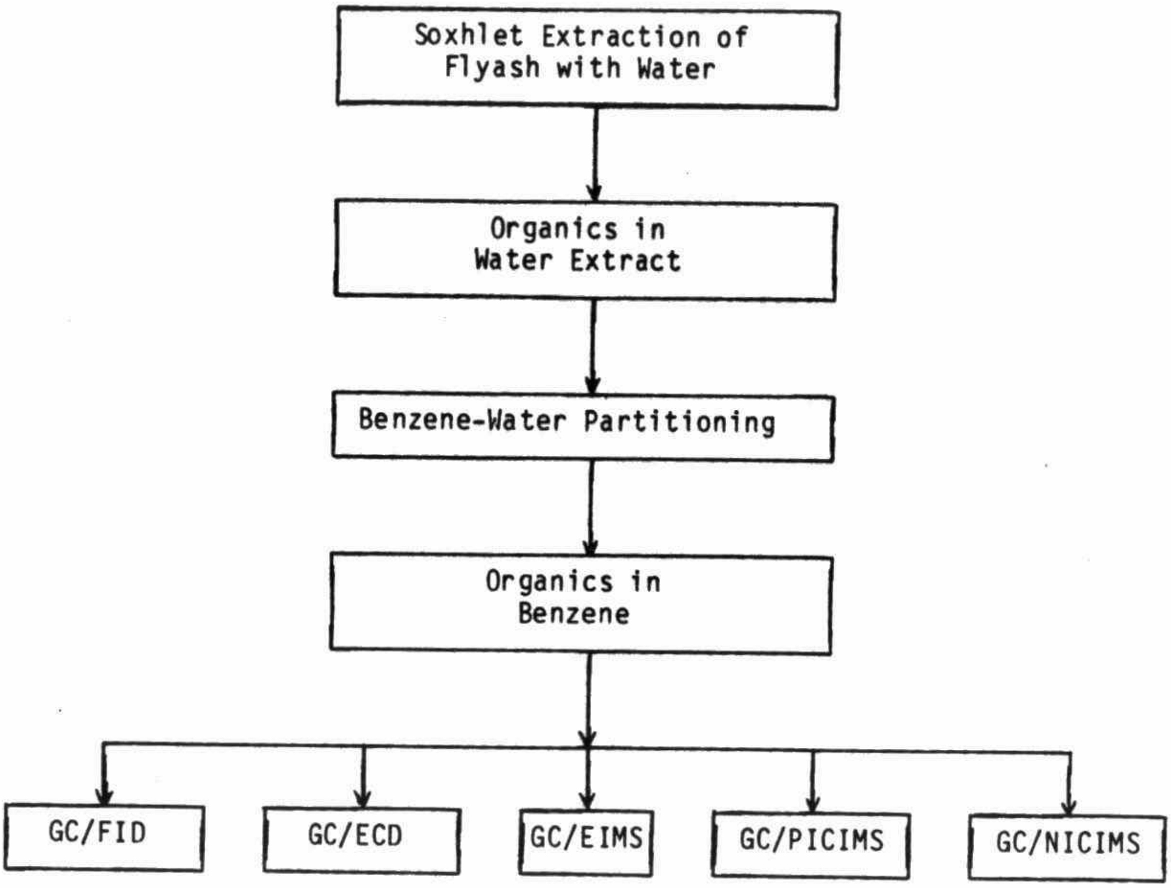
Figure 1: Scheme diagram showing sample preparation procedure and subsequent analysis.

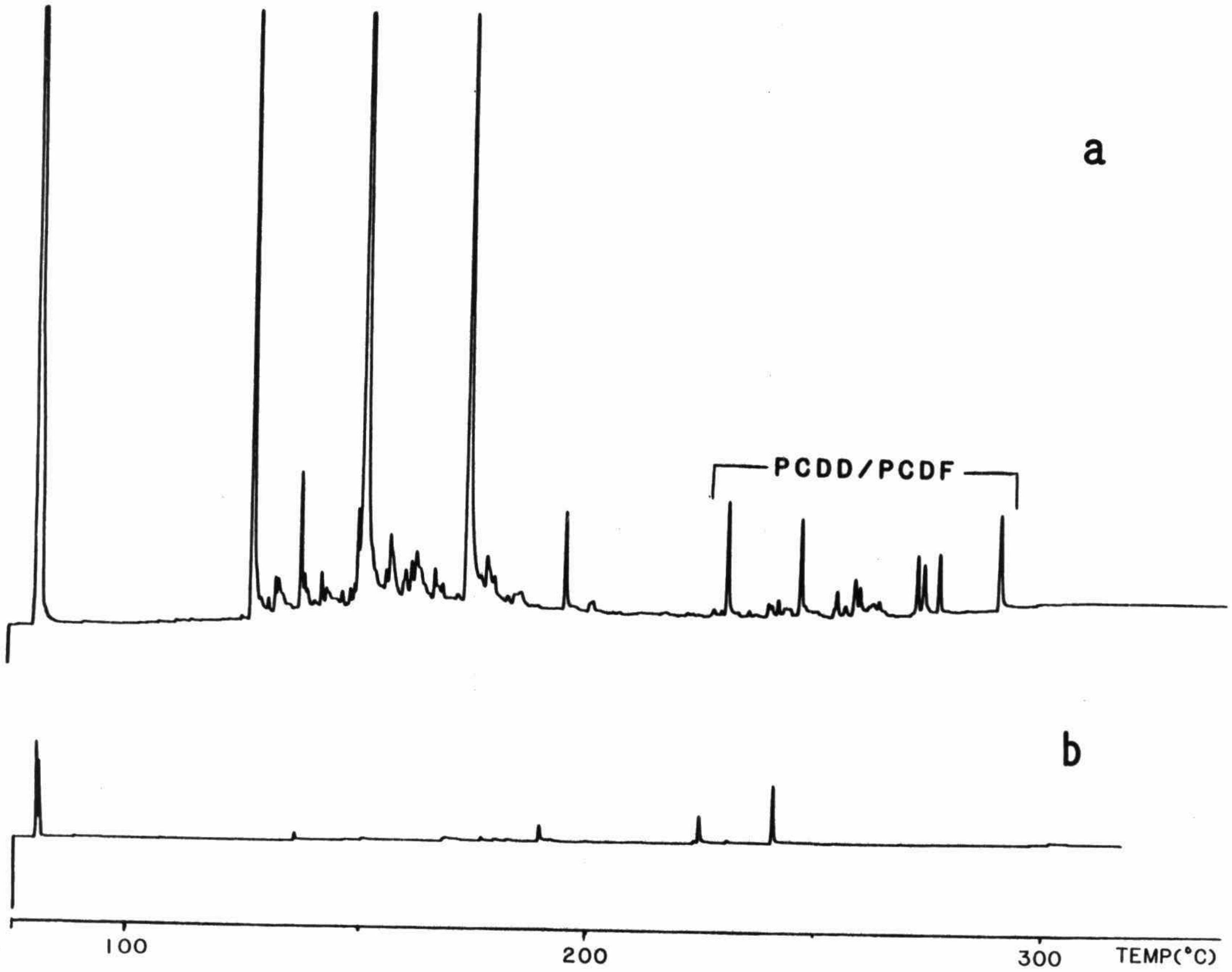
Figure 2: GC/ECD chromatograms of (a) water extract containing PCDD and PCDF, and (b) water extract blank.

Figure 3: GC/NICIMS/SIM data showing the presence of PCDD and PCDF in water extract.

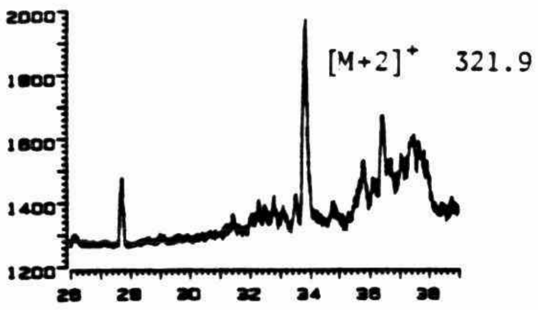
Figure 4: Total ion chromatograms of one water extract analyzed by GC/MS with (a) electron impact ionization, (b) positive ion chemical ionization, and (c) negative ion chemical ionization.

Figure 5: Mass spectra of an unknown compound in water extract: (a) obtained from GC/EIMS, (b) obtained from GC/PICIMS, and (c) obtained from GC/NICIMS.


Soxhlet Extraction of Flyash with Water
Organics in Water Extract
Benzene-Water Partitioning
Organics in Benzene
GC/FID
GC/ECD
GC/EIMS
GC/PICIMS
GC/NICIMS


a
PCDD/PCDF
b
100
200
300
TEMP(°C)

TCDD



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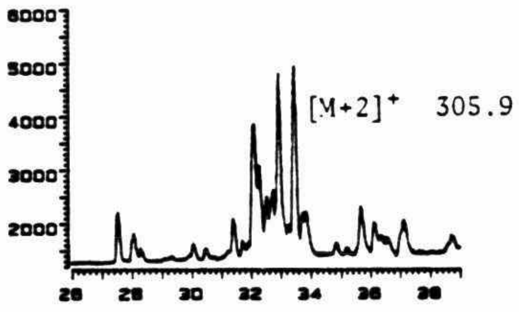
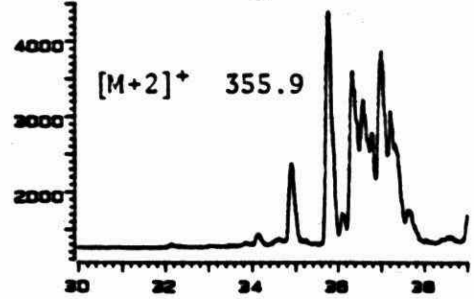


P$_5$CDD



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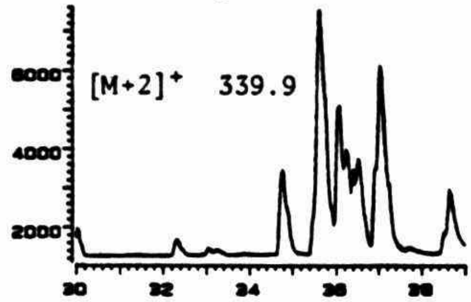

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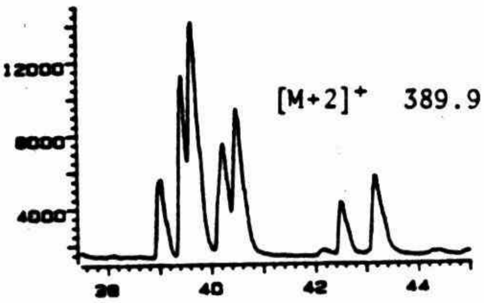

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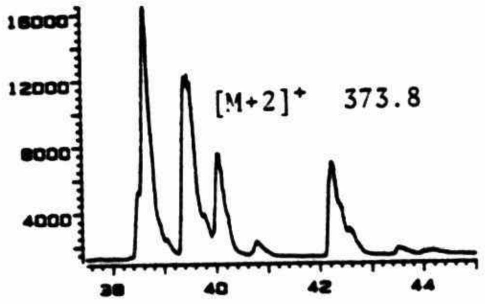

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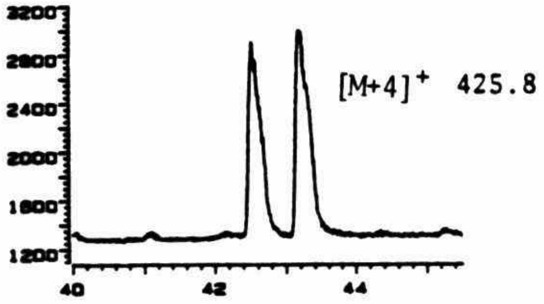

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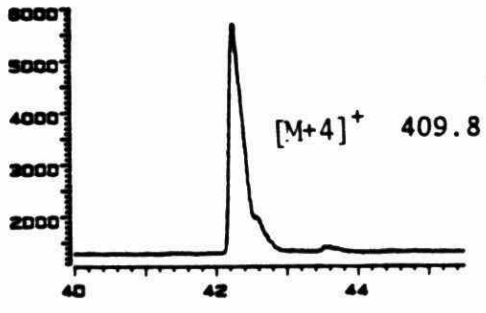

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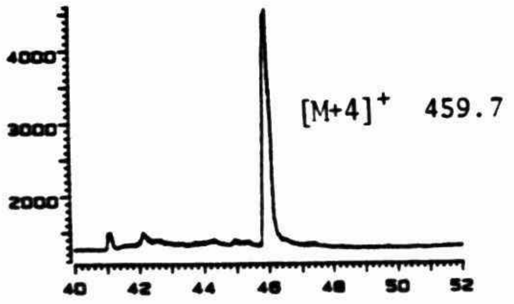

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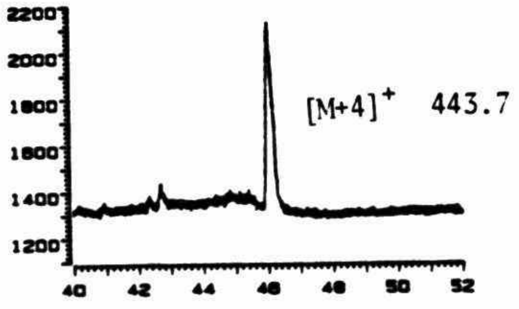

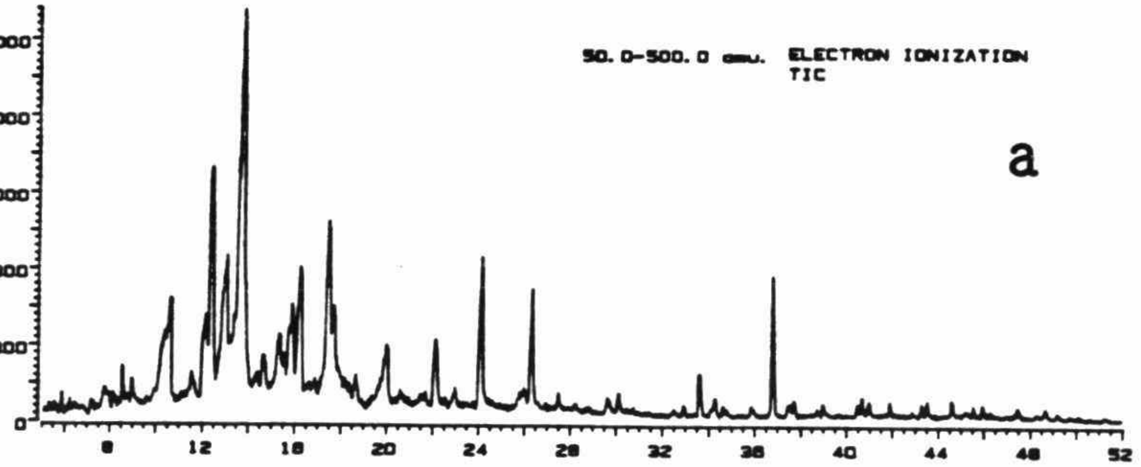
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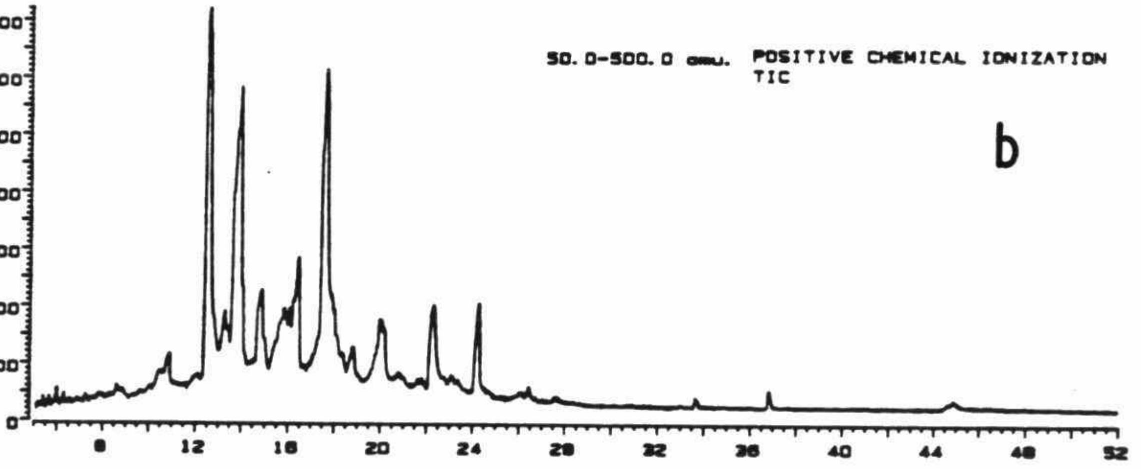
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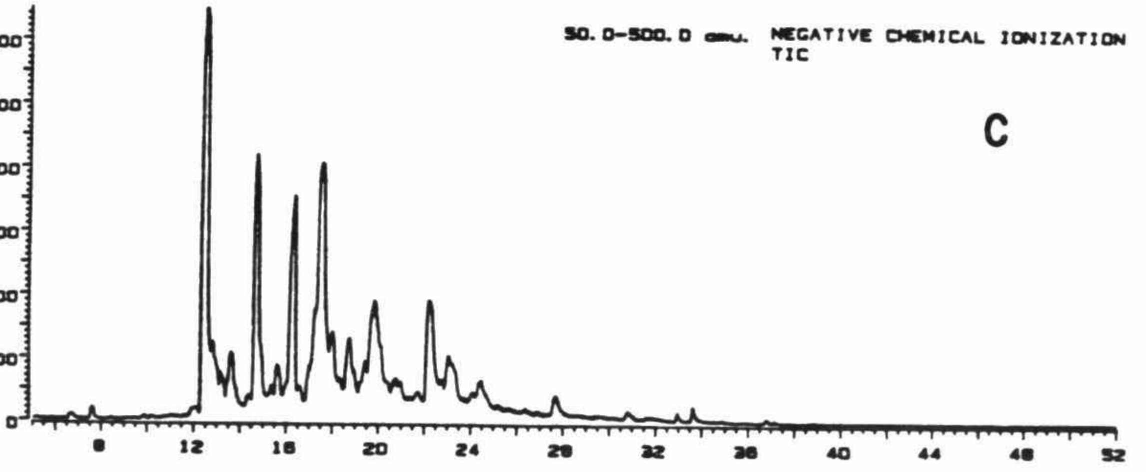
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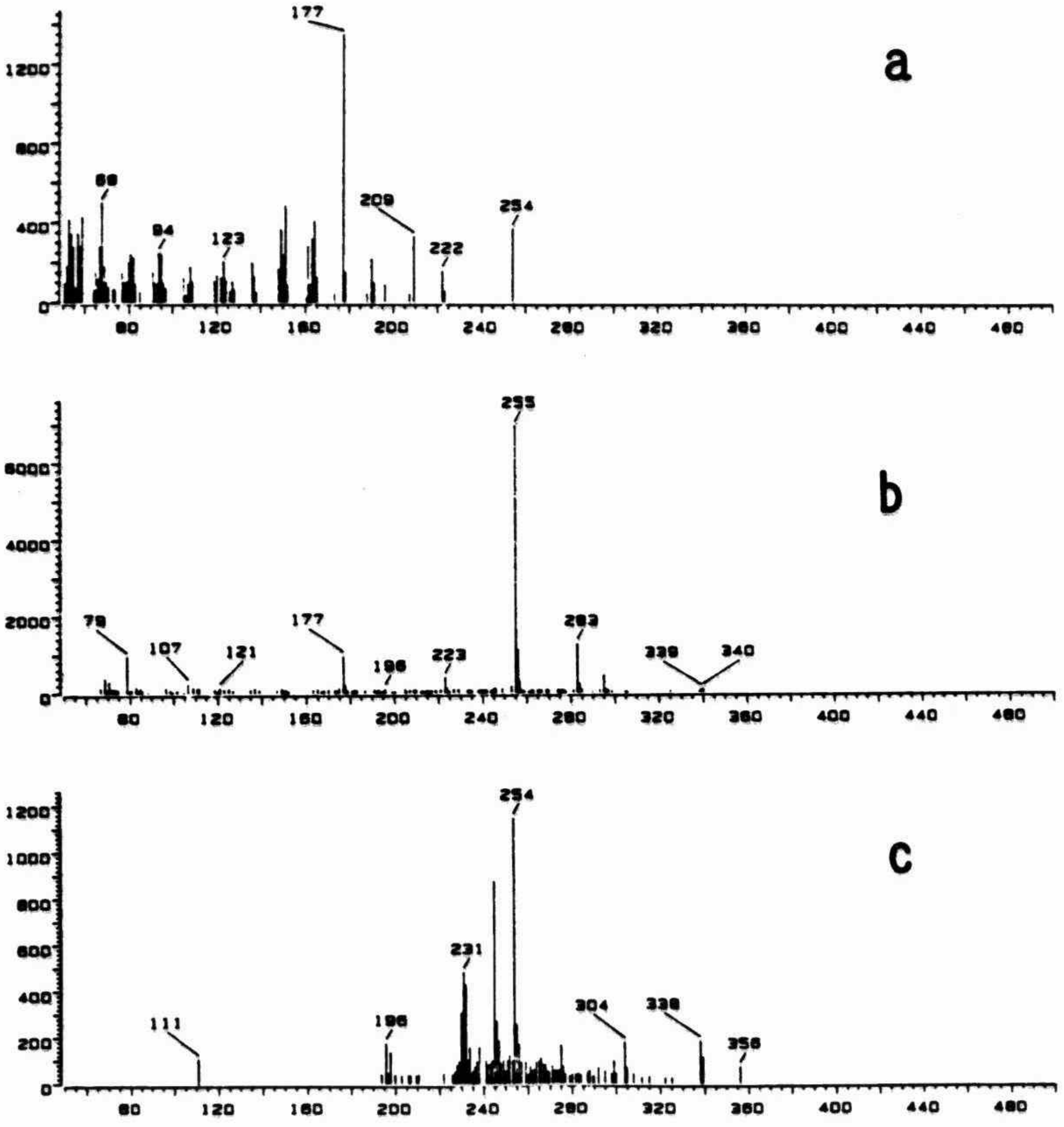
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DEVELOPMENT AND VALIDATION OF PROTOCOLS FOR SAMPLING SURFACE AND GROUNDWATERS FOR ORGANIC CONTAMINANTS

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Key words: Water Quality, Groundwater, Volatile Organics, Water Sampling.

ABSTRACT

In the first phase of this research, present methods of sampling waters, especially groundwaters, for subsequent analysis of volatile organic contaminants were evaluated. The major sources of bias included well flushing procedures, sorption onto sampling equipment and volatilization due to exposure of samples to the atmosphere during sampling.

Following a review of the literature, a series of laboratory experiments were conducted which evaluated the bias and variability of results when groundwaters are sampled by various techniques. The performance of a suction lift system (peristaltic pump) and a gas-drive system (triple-tube sampler) were evaluated. Both systems introduced some negative bias (0.8 to 21.6%) but little variability with standard deviation of less than 10% of the mean. Surprisingly, the suction lift system induced less volatile-loss than the positive-pressure gas-drive system.

It is concluded that monitoring programs should be as standardized as possible. Requirements for well flushing, in particular, may be difficult to establish a priori. For volatile organics, the major source of bias appears to be volatilization loss and so a sampling system which eliminates this loss will be investigated in phase two of this research.

Introduction

Among the most widespread organic contaminants in groundwater are halogenated, one- and two-carbon compounds such as tetrachlorethylene, trichloroethylene, 1,1,1-trichloroethane, chloroform and carbon tetrachloride. These compounds are volatile or semi volatile. Reliable analyses for these contaminants are required to identify the extent of groundwater impact and especially to establish their movement and persistence in groundwater. The latter objective is often met by mathematical simulation of the contaminant transport processes and the quality of the resultant model will depend, in part, upon the quality of the contaminant concentration data.

Variability of volatile organic contaminant data may be natural temporal variability or may be introduced, along with bias, during sampling, sample storage and analysis. This research study is attempting to document the various contributions to concentration variability and bias and then to identify methods to minimize the problems. The major sources of bias and variability in groundwater data that are addressed include:

1. the laboratory analysis
2. collection of unrepresentative groundwater due to inadequate flushing of water standing in the piezometer.
3. volatilization loss during groundwater sampling, especially during filling of sample bottles
4. sorption onto silt often present in groundwater samples

5. chemical or biological transformation (degradation) during sample storage, and
6. natural processes causing real variability of contaminant concentration over time at a sampling well or piezometer

This study combines field sampling with experiments under controlled laboratory conditions. Field sampling was conducted at the Woolwich landfill site near Waterloo where a plume of volatile, chlorinated organics has been identified (Reinhard et al., 1984). Narrow-diameter (1.2 cm or 0.95 cm), bundle piezometers are used at this site, necessitating sampling by a suction-lift system (peristaltic pump) or a gas-drive system (triple tube sampler, Robin et al., 1982). Most results to date were reported by Travis and Barker (1985), but this paper also presents more-recent results.

Analyses

Volatile organics were determined by a micro-solvent-extraction technique modified after Glaze et al. (1983). Details are presented by Mackay et al. (1985). Briefly, the aqueous sample is collected in 60 cm^3 hypovials with a crimped, teflon-faced septum seal. Using separate syringes, 1 cm^3 of groundwater is removed and 0.5 cm^3 of pentane containing m-fluorotoluene as an internal standard is added. The vials are shaken, allowed to stand and an aliquot of the solvent phase injected into either a gas chromatograph (GC) or gas chromatograph/mass synctrometer (GC/MS) where the components are resolved with a capillary column and detected by electron capture or mass spectrometry. Standards, consisting of distilled water spiked with a methanol solution containing the organics and the internal standards, are processed in the same manner. Typical quality assurance information is summarized in Table 1.

Table 1: **Pentane Extraction** - Volatile Organics Quality Control Information

METHOD DETECTION LIMIT - Reagant water matrix

Cmpd	#aliquots	$\overline{X}$	X_o	S%	E%	MDL
Chloroform	7	1.56±0.14	1.41	8.9	+11	0.44
1,1,1 Trichloroethane	7	1.00±0.02	1.03	2.1	-2.6	0.06
Carbontetrachloride	7	1.00±0.04	1.29	3.9	-22	0.12
Trichloroethylene	7	1.16±0.03	1.08	2.3	+7.0	0.09
Tetrachloroethylene	7	2.24±0.06	2.17	2.8	+4.0	0.20

ACCURACY AND PRECISION AT TYPICAL SAMPLE CONCENTRATION - Reagant water matrix

Cmpd	#aliquots	$\overline{X}$	X_o	S%	E%
Chloroform	10	32.32±0.83	29.72	2.6	+5.8
1,1,1 Trichloroethane	10	21.38±0.36	21.78	1.7	-2.0
Carbon tetrachloride	10	28.17±0.41	28.43	1.5	-1.0
Trichloroethylene	10	22.62±0.37	22.85	1.6	-1.0
Tetrachloroethylene	10	48.45±0.76	45.79	1.6	+5.8

$\overline{X}$: mean of replicate determinations, 99% confidence level
X_o : true value
S% : relative standard deviation
E% : relative error
MDL : method detection limit

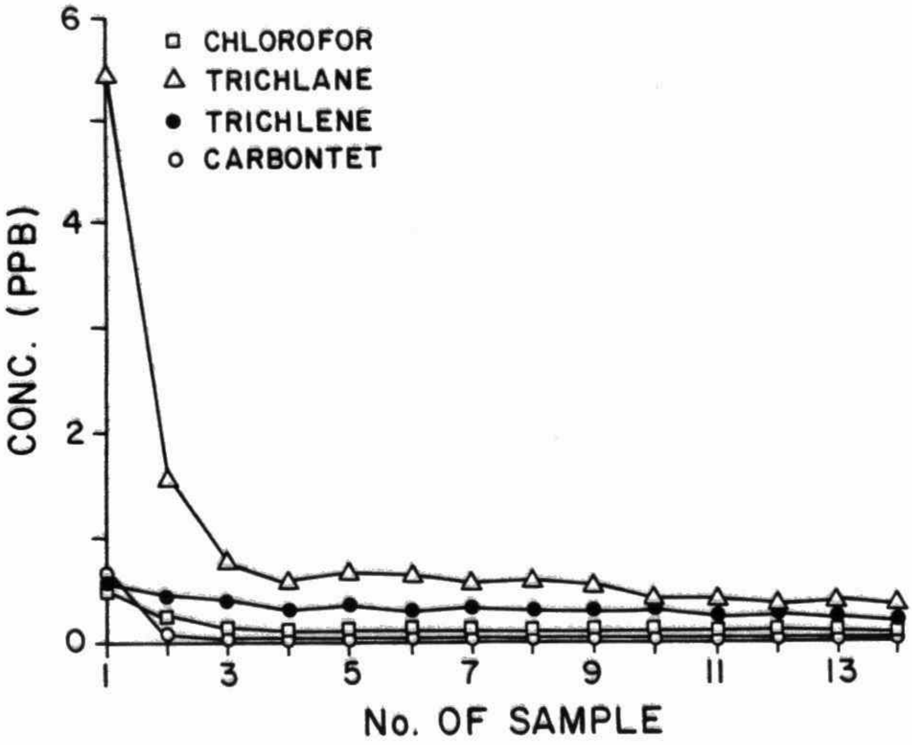
Piezometer Flushing

Water standing in a piezometer or well is generally deemed unrepresentative of groundwater in the aquifer adjacent to the screened intervals so it must not be included in any sample taken (Gillham et al., 1983). Normally the standing water is removed or flushed by removing from three to ten times the standing water volume to draw in fresh representative groundwater. The amount of flushing is arbitrary, based on "experience" (Gibb et al., 1981, for example), and without a firm scientific basis (Gillham et al., 1983).

The affect of piezometer flushing upon the resultant concentration attributed to the groundwater is illustrated in Figure 1. The triple-tube sampler was employed. Essentially all the standing water is removed during each sampling cycle and the cycle was repeated at 0.5 h intervals. At this piezometer, only 1,1,1-trichloroethane (1,1,1-TCE) was present at significant concentrations and its concentration is seen to dramatically decrease over the flushing of 4 standing volumes and then to remain essentially constant. If these results can be generalized, it would appear that significant variability in data from repeated sampling of a piezometer could be induced by collecting samples after variable numbers of flushing cycles. This suggests standardized sampling protocols are essential to obtain comparable data.

Unfortunately, since the true groundwater concentration cannot be defined without sampling (a source of bias) it is not possible to decide whether the initial water or the water collected after 4 flushing cycles is most representative - a situation not unlike that which lead to Heizenburg's uncertainty principle in atomic physics. Generally, the lower concentrations, obtained after considerable flushing, would be taken as most representative. What, then, is the cause of the initially high 1,1,1-TCE values? It was speculated by Travis and Barker (1985)

Figure 1: The Concentration of Volatile Halocarbons In Sequential Piezometer Volumes Removed With the Triple-Tube Sampler



that this high concentration in water standing in the piezometer resulted from contaminants in the leachate plume above the sampled depth diffusing through the polyethylene piezometer walls into the standing water (Figure 2). Polyethylene is permeable to aqueous organics, as shown by experiments conducted with monoaromatics as mentioned by Patrick et al. (1985). In 1984, samples could not be drawn from depths above the 4th point in piezometer ML 16, but the piezometer was resampled in 1985. Groundwater above the 4th point contained only from 1.7 to 1.2 ug/l 1,1,1-TCE. Repeated sampling of ML 16-4, similar to that shown in Figure 1, revealed an erratic 1,1,1-TCE concentration pattern ranging from an initial value of 0.1 ug/l to sporatic later values of 1.6 ug/l. Thus the problem illustrated in Figure 1 has not persisted from 1984 to 1985. Unfortunately, the 1984 results cannot be discounted, since a "slug" of high-concentration could have moved past ML 16 by 1985.

The long-term variability of trace, volatile organic contaminant concentration data, illustrated in Figure 3 for another piezometer point at Woolwich (ML 3-3) may be due, in part, to non-uniform piezometer flushing protocols. However, even when a constant protocol of flushing 3 standing volumes before sampling is employed, considerable variability persists as shown in Figure 4.

Figure 2: Hypothetical Groundwater Contaminant Distribution Leading to Contamination of Water Sampling in a Piezometer

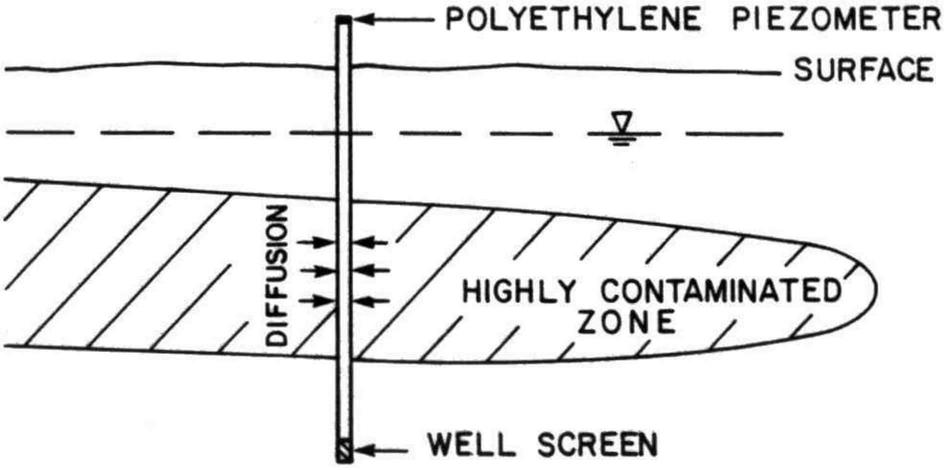


Figure 3: Variation in Volatile Halocarbon Concentrations in Samples from Piezometers ML 3-3: 1982-84

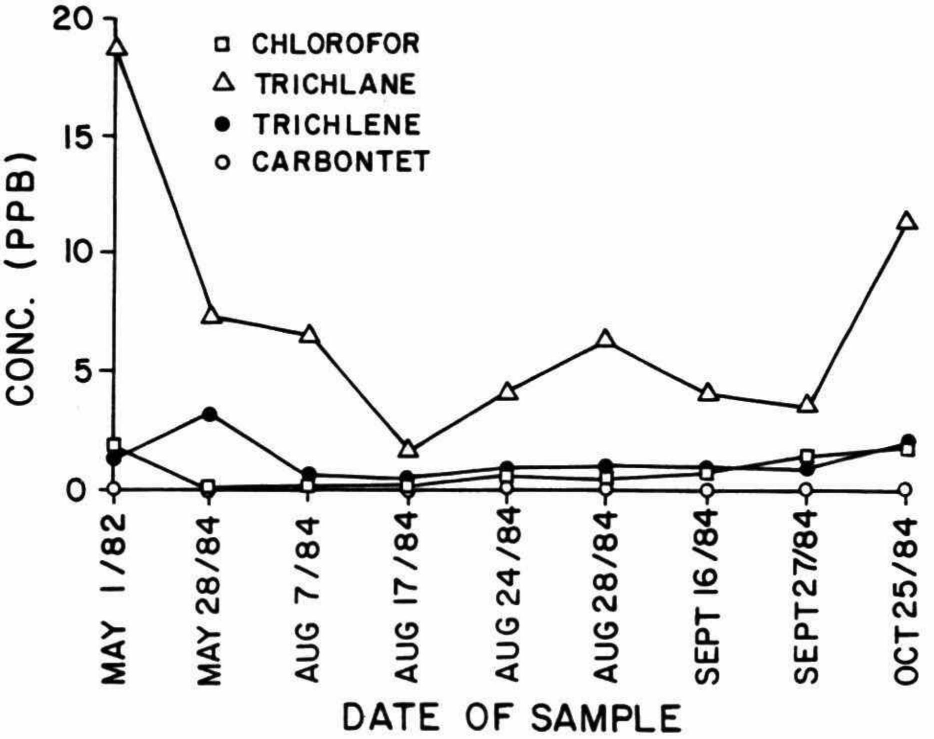
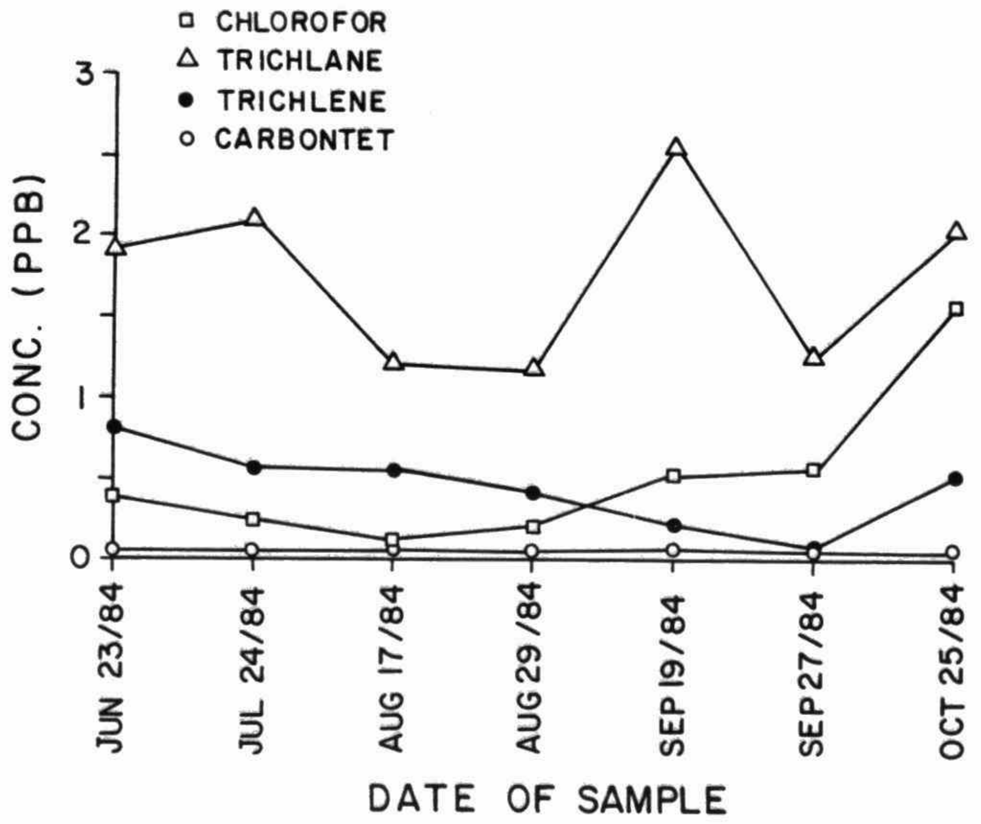


Figure 4: Variation in Volatile Halocarbon Concentration in Samples from Piezometer ML 16-4: June, 1984 to October, 1984



Volatilization Loss During Sampling

Exposure of groundwater to a gas phase during sampling permits the possible loss of volatile organics to the gas phase. Applying suction during sampling with the peristaltic pump should enhance volatilization losses. The triple-tube sampler employs a gas-drive and so exposes some of the water being brought to the surface to a gas phase. Unfortunately, the extent of any losses cannot be assessed in the field because the true groundwater concentration is not known.

A series of laboratory experiments, representative of field sampling situations, were undertaken. Water, spiked with organics in the range of 4 to 32 ug/l, was sampling from teflon tubing attached to a teflon bag which acted as the reservoir. The reservoir was placed under water to force about 1 m of spike water into the teflon tubing to represent a piezometer with standing water. This tubing was extended upwards about 5.5 m and water was sampled from the tubing alternatively with a peristaltic pump attached to the teflon tubing and with a gas-drive system similar to the triple-tube sampler. In addition water was drawn from the reservoir with a gas-tight, glass-teflon syringe. All water was transferred into hypovials for analysis. Thus, a comparison of results from water sampled from the tubing to results from water drawn from the reservoir permits an evaluation of bias and variability induced by these sampling methods. Volatilization loss from the hypovials prior to capping is constant and undoubtedly minor for all three types of samples.

Figure 5 presents some of the results. In all cases, the samples drawn directly from the reservoir had the highest concentration suggesting both gas-drive and suction-lift sampling induces a negative bias probably due to volatilization loss. Negative bias, relative to the reservoir sample, ranged from 0.8 to 13.7% for the triple-tube sampler and from 4.2 to 21.6% for the peristaltic pump sampler. Table 2 presents the results for more volatile organics at higher concentrations. Surprisingly perhaps, the relative negative bias of the peristaltic pump system was only 0 to 5% while that for the triple-tube system was 12 to 19%. In general, the variability of replicate samples collected with the triple-tube system (about 10% standard deviation) was greater than with the peristaltic pump.

Clearly, comparing results of samples collected by different systems could be misleading. The triple-tube sampler was always used at the field site. Thus the field results (Figures 3 and 4) are expected to suffer a negative bias by up to 19% and a variability of perhaps 10% could be attributed to this sampling method. The combination of analytical and sampling-system variability does not account for the major portion of temporal variability illustrated in Figure 4.

Figure 5: Mean Sample Concentrations Where a Reservoir (Standard) was Sampled with a Peristaltic Pump (Peristaltic) or with a Triple-Tube Sampler (TRPL TUBE)

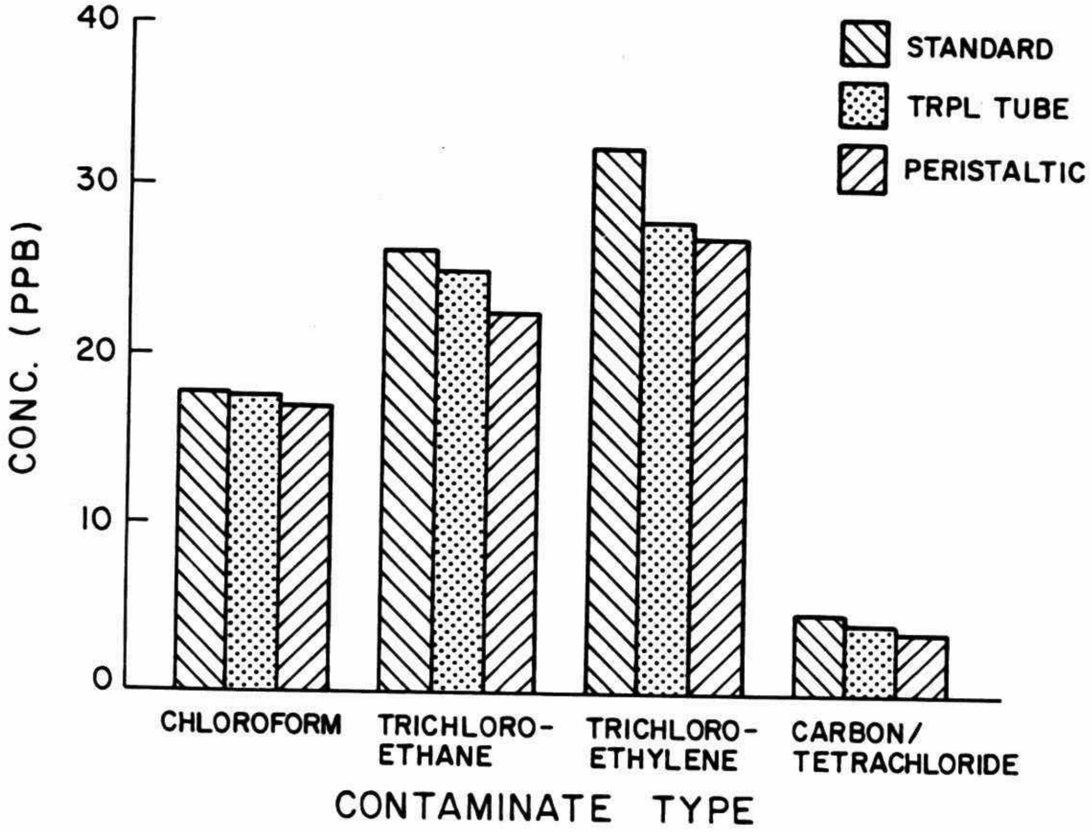


Table 2: A Comparison of Concentrations in a Reservoir (Standard) and in Samples Obtained with a Triple-Tube Sampler or a Peristaltic Pump

CHEMICAL	Triple-Tube		Peristaltic		Standard	
	Mean	Stan. Dev.	Mean	Stan. Dev.	Mean	Standard
1,2 Dichloroethane	140.8 PPB	16.24	161.8 PPB	11.8	161.5 PPB	7.1
Methylene chloride	369.6	50.2	430.8	27.7	429.5	11.7
1,1 Dichloroethylene	260.5	48.3	304.1	24.2	320.6	12.8

Sorption Onto Silt

Water drawn from wells or piezometers almost always contains silt- or clay-size solids which are small enough to pass the well screen. If organic contaminants are sorbed onto this material, and if the subsequent solvent extraction will recover most, then the additional concentration would be attributed to the groundwater itself. This could be a serious positive bias. Filtering of the groundwater is not usually advised for volatile organics which may be volatilized or sorbed during filtration. Variable amounts of silt in replicate samples could introduce a variable bias. On the other hand, the silt could act as a sorbant and could remove organics from the water so that subsequent analyses would be negatively biased. This would be more likely with "purge-and-trap" analyses than with solvent extraction analysis. The latter should be more efficient in removing sorbed organics. Silt was commonly found in groundwater samples from Woolwich, so calculations were performed and a laboratory experiment was established to evaluate its presence as a source of bias and variability.

Homogenized silt, collected from previous groundwater samples, was baked at 250C to remove sorbed, volatile organics. Various quantities (0, 0.25 and 0.5 g) was added to replicate hypovials which were then filled with water spiked with 26 to 84 ug/l of each of four halocarbons. Samples sat for 48 hours prior to extraction and analysis. No significant variation (< 3%) in organic concentrations for various silt contents was found. It was therefore concluded that the presence of silt was not causing a significant bias in the subsequent analysis.

The possible addition of organics to the aqueous analysis in the form of sorbed organics was evaluated by a mass balance calculation. The distribution of an organic between the aqueous phase and sorptive sites on the solids is expressed as a distribution coefficient, Kp, where the aqueous concentration (C) is in ug/l and the sorbed concentration (S) in ug/kg soil.

$$Kp = S/C$$

For hydrophobic organics such as those considered in these experiments, the Kp can be predicted from hydrophobicity data and the fraction of organic carbon (foc) present in the solids using regression-fit equations (Karickhoff, 1984). The foc of the silt was about 0.0005 and the estimated Kp for carbon tetrachloride (CTET) was about 0.1. Thus if there was 60 ug CTET in solution in the hypovial only 10^{-2} ug CTET would be present on the 1 g of silt - an insignificant addition to the aqueous concentration.

Thus it is concluded that the presence of silt is an insignificant source of bias or variability for these organic contaminants.

Sample Degradation During Storage

All groundwater samples were kept on ice ($4^{o}C$) and in darkness prior to analysis. Samples collected in 1985 also received about 10 ug of a 10% sodium azide bacteriacide solution. Previous studies (Reinhard et al., 1985; Patrick et al., 1985) found that neither volatile halogenated nor volatile monoaromatic organics changed concentrations over the one- or two-week storage time commonly required prior to analysis when maintained under these conditions. Therefore this was not considered a significant cause of bias in this study.

Conclusions - Natural Variability

In studies of groundwaters from the Woolwich landfill site, contaminated by volatile halocarbons, laboratory experiments identify the piezometer flushing protocol and sampling system (induced volatilization) as the major sources of bias. Insufficient piezometer flushing could produce a significant positive bias of up to 100% in some organic concentration data. The sampling system could produce up to a 19% negative bias. Other sources were considered far less important.

Variability or reproducibility of results is difficult to assess because there is no proof that a homogeneous concentration is present in groundwaters. However, laboratory experiments suggest that the major source of variability is inherent in the triple-tube sampling system. Expressed as relative standard deviation of replicate samples, this source may introduce about 8% variability. It should be noted that the bias resulting from inadequate piezometer flushing could also express itself as variability among sequentially-collected, "replicate" samples.

Ignoring this possibility, the sum of the analytical and other sources of variability would be about 15%, expressed as the relative standard deviation.

How does this compare to the observed, temporal variability of volatile organic concentration data? Figure 4 indicates the changes in concentration observed at piezometer point ML 16-4 for a four month period. A consistent sampling protocol was employed. Trichloroethylene concentrations have a mean of 0.44 ug/l and a relative standard deviation of 54%, and 1,1,1-trichloroethane a mean of 1.8 ug/l and a relative standard deviation of 30%. This variability is beyond that expected due to procedural limitations and therefore a major portion is considered natural, temporal variability.

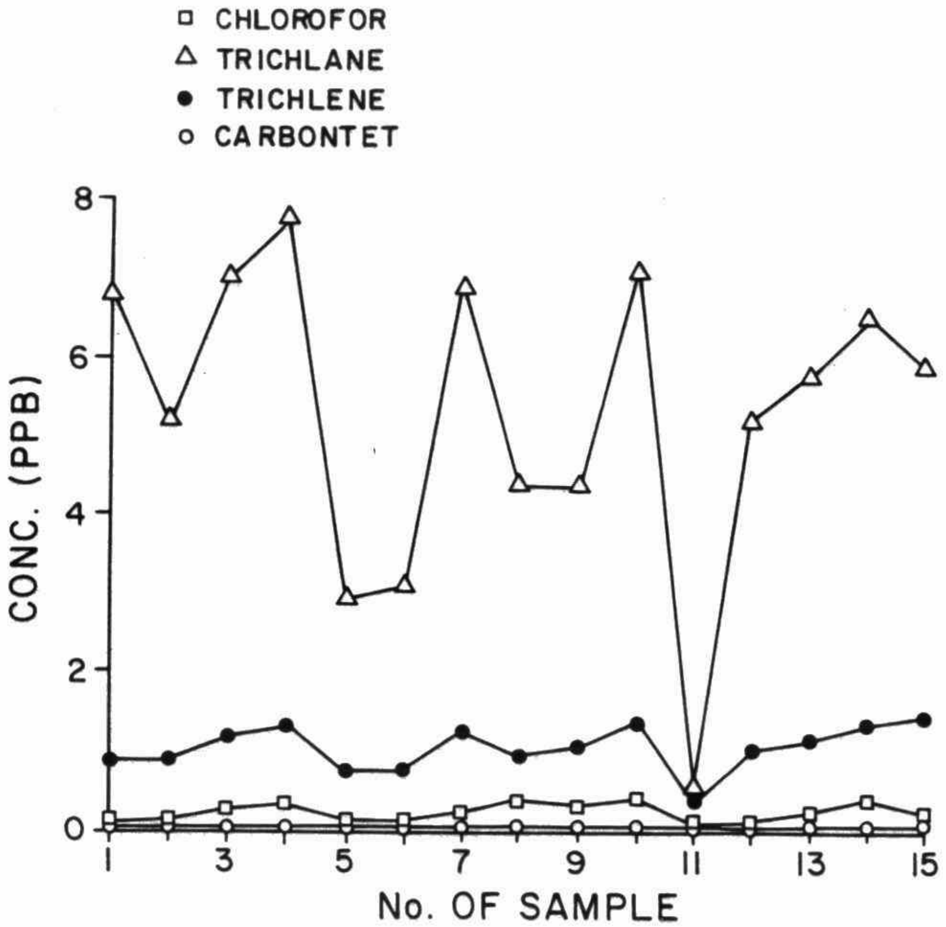
Figure 3 presents the variability at another piezometer point ML 3-3 over a longer time (2.5 y). Again, 1,1,1-trichloroethane concentrations are highest, with a mean of 7.1 ug/l and a relative standard deviation of 73%. A portion of this variability could be attributed to inconsistent well flushing protocols as well as to greater, natural temporal variability over the longer time.

Temporal variability over short periods is also greater than should be attributed to sampling and analytical limitations. Figure 6 presents the results for samples collected over a 7.5 h period at 0.5 h intervals. For 1,1,1-trichloroethane, the mean concentration ws 4.4 ug/l and the relative standard deviation was 43%.

The relative standard deviation of 1,1,1-trichloroethane increased from 43% from sampling over 7.5 h, to 54% for sampling over 4 mo, to 73% for sampling over 2.5 y. Thus, variability seems to increase over the sampling time span.

Given the normal uncertainties in hydrogeological transport rate estimates (+ 20 to 100% perhaps), the bias introduced in these volatile organic contaminant measurements are not likely to be the greatest source of error in transport modeling. Although this bias could exceed +100% with inconsistent piezometer flush-

Figure 6: Concentrations of Volatile Halocarbons in Samples Collected Each 0.5 Hour from Piezometer ML 3-3



ing, a bias of less than -25% due mainly to volatile loss during sampling is more likely, given consistent sampling procedures. This magnitude is similar to the bias reported for a wide-range of sampling methods (bailers, positive-displacement pumps, etc.) by Barcelona et al. (1984). Improvements in volatile, organic data quality could be made when systematic sampling procedures are followed rigorously and when loss by volatilization is minimized. Although a prototype improved sampling system, designed to eliminate volatilization is to be developed and tested, another situation in which volatilization could be even more important will be addressed in 1985/86.

Current research is concentrating upon the possible loss of volatile organics from water standing in wells and piezometers installed in low-permeability formations. In such aquitards, it is often necessary to remove standing water and then wait hours to weeks for sufficient recharge to permit sampling. It is anticipated that greater volatile loss will occur in such wells and so current efforts are directed to its evaluation and possible reduction.

Acknowledgements

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LABORATORY STUDY OF TILE DRAIN EFFICIENCIES FOR LEACHATE COLLECTION

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Key words: Tile Drainage, Leachate, Leachate Collection, Hydraulic Characteristics.

ABSTRACT

A physical 2-dimensional model using a homogeneous and isotropic sand medium, with water as the fluid, was tested to determine the effectiveness of tile drain systems in capturing groundwater recharge from infiltrated precipitation. For a landfill, this recharge is leachate. Experiments were conducted for configurations with varying hydraulic gradients, position of the tile within the flow field, thickness of the flow field, tile spacing and recharge rate. All experiments were for the steady state condition.

Original gradients were established by varying both the recharge rate at the upper surface and the hydraulic head in a permeable "aquifer" that formed the lower boundary of the model.

The ratio of flow that bypassed the tile drain(s) to the total recharge (input) to the system (Q_A/Q_R) is a measure of the efficiency of the tile system for leachate collection.

Graphs of Q_A/Q_R vs R/K_s (recharge/saturated hydraulic conductivity) for different positions of the tile drain(s) and spacing of tile drain(s) (H_D/L), show that unless the tile is placed at an elevation below the hydraulic head in the aquifer, some water (leachate) will bypass the collection system.

In our model studies, the water table is a consequence of the parameters of the medium and the experimental conditions but the position of the water table is not a factor in evaluating the performance of the tile drain(s).

Introduction

In humid or sub-humid regions like Southern Ontario, the production of leachate within sanitary landfills is an inevitable consequence of infiltration of water through the surface cover, and the interaction of this water with the buried waste. Leachate characteristically contains concentrations of dissolved matter far in excess of drinking water standards. Therefore, landfills must be considered as potential sources of groundwater contamination, and this must be a consideration in landfill siting and design.

Proper placement of a landfill with respect to the hydrogeological setting including the groundwater flow system, the properties of the subsurface materials and the proximity of aquifers and surface water are key factors in avoiding serious contamination.

For new landfill sites in Ontario the risk of groundwater contamination must be evaluated, with leachate strength, rate of production and rate of flow being important considerations. It is now accepted practice to use a clay cover to minimize leachate production by reducing infiltration into the landfill. In some cases a tile drain system under the refuse is used to capture leachate to prevent or reduce groundwater contamination. Questions are then raised as to the effectiveness of a given design in terms of intercepting leachate.

A great deal has been published on the use of tiles for drainage of agricultural lands. Almost all published work on this topic relates to the central problem of lowering the water table to allow for cultivation of the land, in which case the downward leakage of groundwater between drains is of little consequence (Childs (1943), Collis-George and Youngs (1953), Engelund (1951), Kirkham and De Zeuw (1952), List (1964), Youngs (1974), and Youngs (1975). In the case of leachate collection under landfills, the amount of groundwater that by-passes the tile collectors is the main concern and the lowering of the water table is of no importance except as it relates to this bypass. The use of an impermeable liner at the bottom of the landfill is often proposed and designs for tile drain systems with liners have been investigated and described by several authors including Wong (1977), McBean et al. (1982) and Demetracopoulis et al. (1984). The purpose of this study is to examine the effectiveness of tile drain systems for collecting leachate from landfills without liners, hence much of the analysis in the literature involves boundary conditions not particularly relevant to the scenario investigated here.

A physical 2-dimensional model using a homogeneous and isotropic sand medium was used with water as the fluid. Experiments were conducted for particular drain configurations by varying both the drain height above an arbitrary datum and the horizontal drain spacing, for a series of controlled hydraulic gradients and precipitation rates. The physical model was intended primarily to verify the results of a numerical model being developed to simulate flow towards drains placed beneath a landfill for a variety of geologic and hydraulic conditions. Work on these two types of models comprises the first year of a three-year research project funded by MOE-Lottery fund. The intent for Year One is to provide a sensitivity analysis of collection efficiencies for tile drains in very idealized hydrogeologic conditions. In Year Two and Year Three, studies of more realistic variables such as anisotropy and layering will be examined.

Method

The experiments were conducted using a rectangular plexiglass box 120 cm high, 140 cm long and 8 cm wide (Fig. 1). A half cell approach was used to approximate the boundary conditions that would exist around a drain network placed under a landfill. The upper surface represents a water table boundary in an unconfined system. The two side boundaries represent the no-flow boundaries that one would expect directly below an operating drain and at the hydraulic divide between two adjacent drains in a symmetrical drain field. The half cell does not address the problem of regional flow towards the drains located at the outer edges of the landfill. The bottom 10 cm was packed with #10 grade silica sand with a saturated hydraulic conductivity (Ks) of 2.5×10^{-1} cm/sec. This material was overlain by 106 cm of Chalk River medium-fine grained sand with a saturated hydraulic conductivity (Ks) = 5.0×10^{-3} cm/sec (Sudicky 1985). The medium-fine sand was mixed during emplacement to minimize horizontal stratification as an attempt to achieve isotropic test conditions. The lower aquifer was used to allow for specific gradients to be set between a zone at depth and the operating drain(s), and to allow the fluid that bypassed the drains to escape the system and be measured. The high permeability of this layer was assumed to make the influence of the impermeable base plate of the model negligible.

The experiments were evaluated for steady state flow under uniform recharge conditions. No attempt was made at this stage to evaluate drain performance for the transient conditions of recharge one would expect in the field.

Drainage was achieved through a symmetric arrangement of valved drains at both ends of the box. The drains were constructed of 0.9 cm ID split plexiglass tubing, perforated and screened, and set flush with the end plate across the width of the box (Fig. 2). The drains were at heights of 5, 25, 45, 65 and 85 cm above the underlying silica sand layer. Drainage and hydraulic head in this lower "aquifer" was controlled through four drains connected to a constant head reservoir mounted outside the box.

Recharge was simulated by a "rainulator" which comprised a tank drained by 0.56 mm ID stainless-steel tubes on a square grid of 2.6 cm, mounted over the entire surface of exposed sand. A range in rainfall intensities of 0.25 - 3.0 cm/hr was possible by adjusting an overflow tube which controlled the water level in the rainulator.

Hydraulic head in the sand was monitored by 21 manometers set in the face plate and end plates of the box. The manometers were placed flush with the interior of the box and screened with 100 x 100 stainless steel mesh.

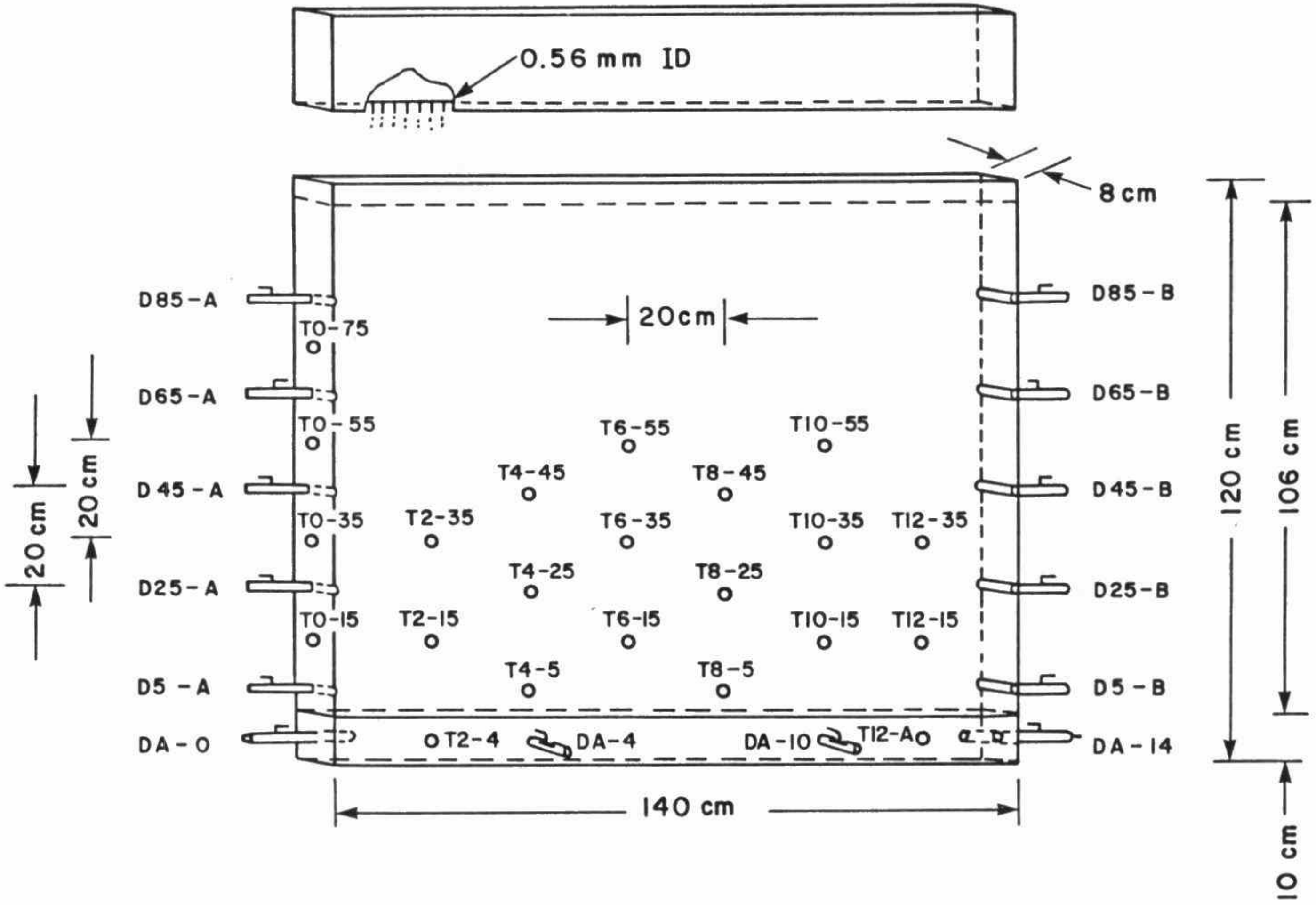


Figure 1: Laboratory model dimensions.

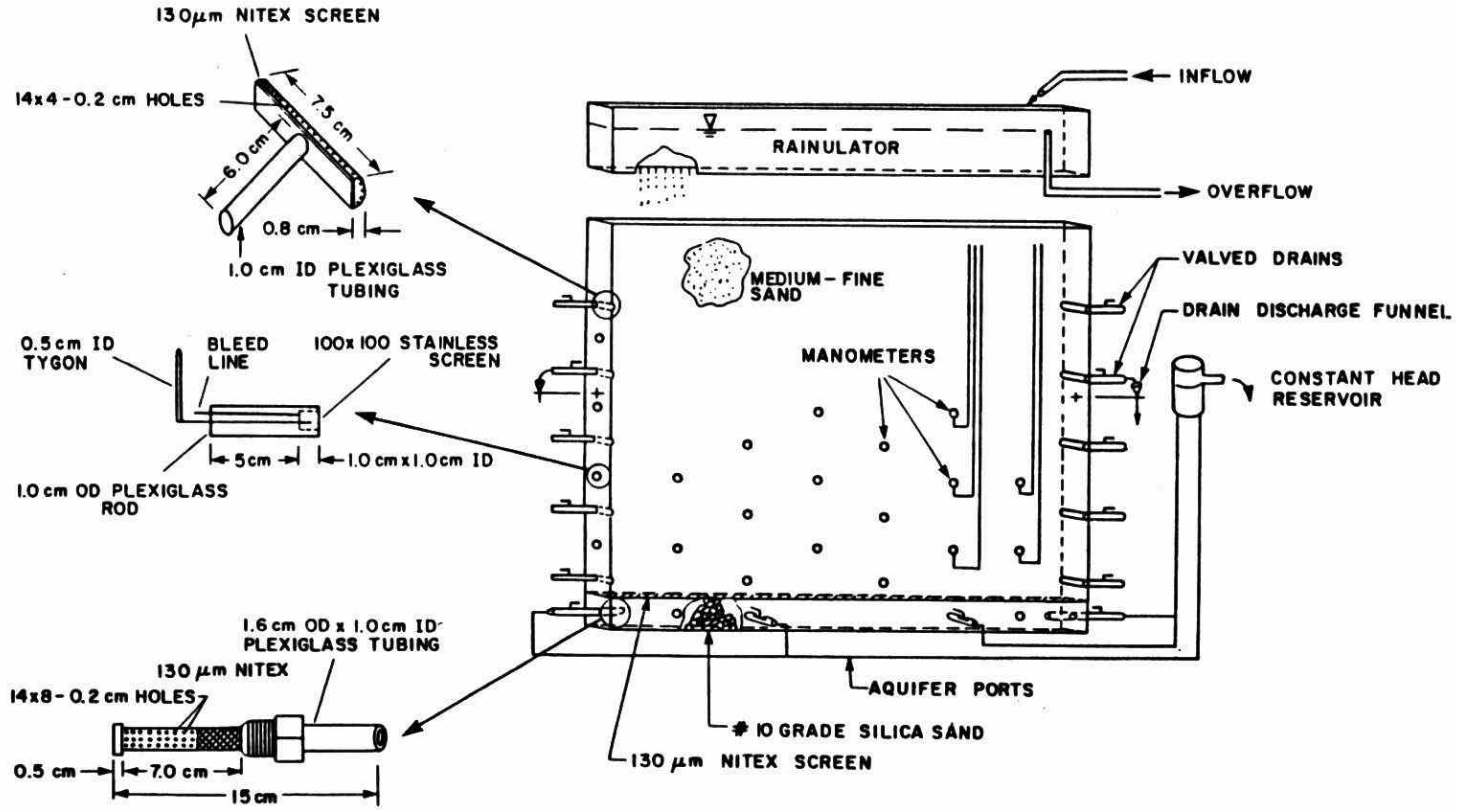


Figure 2: Experimental apparatus.

Procedure

Tests were conducted by deciding on a drain position (H_D; at which pressure head (ψ) = 0, so hydraulic head at drain (H_D) = Z (elevation) and a drain spacing 2L (either 140 cm or 280 cm dependent on whether a drain was open at one - or both ends of the box). The sand was then saturated from the bottom (to minimize air entrapment) until a high water table was established. The rainfall rate R, was first adjusted and measured using a collection trough, before being applied to the surface of the sand. The volumetric rate of inflow to the system, Q_R, was the product of the rainfall rate (R) and the area of the upper surface of the sand. The rainfall rate was checked again at the end of each test.

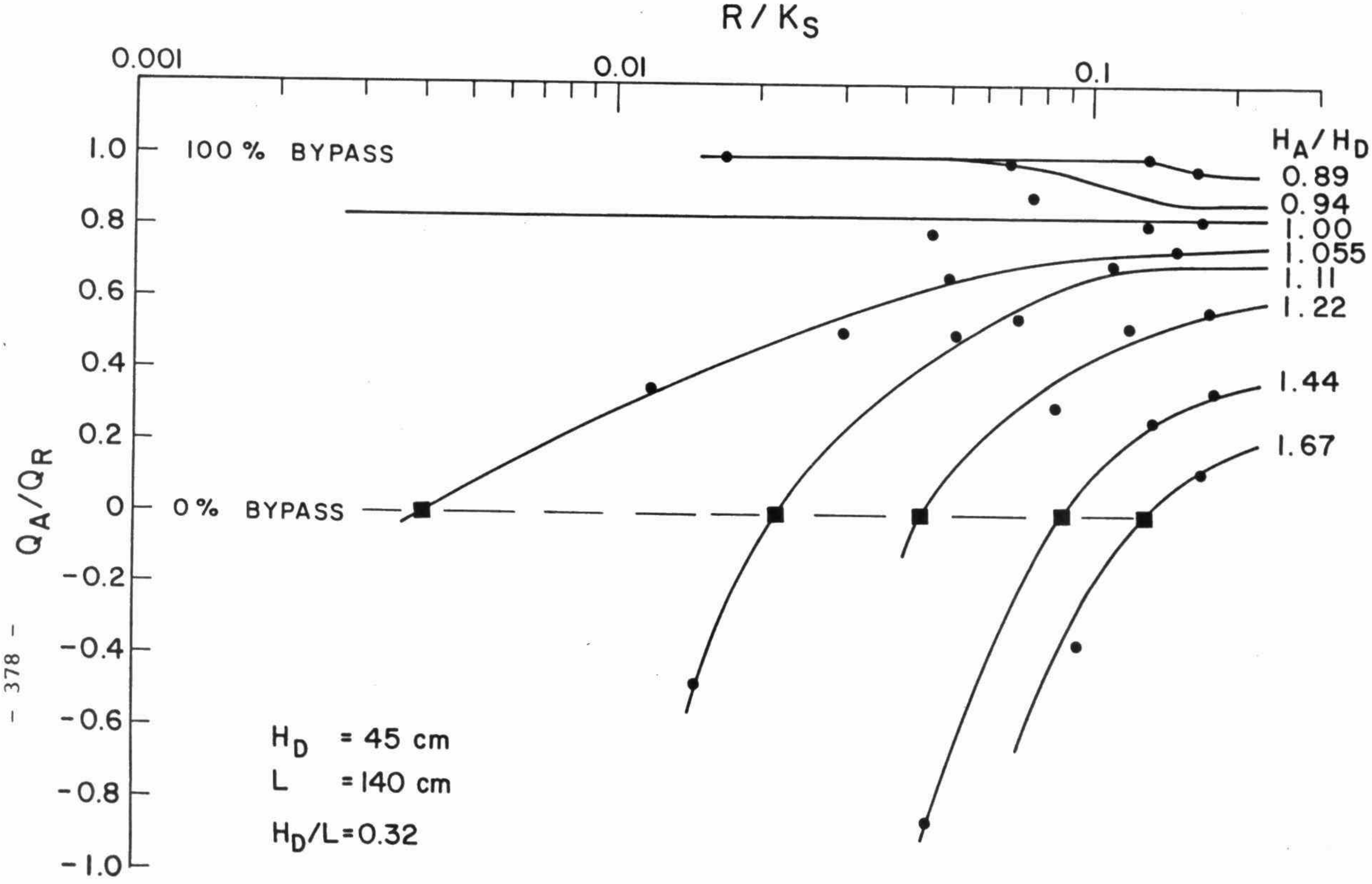
The head ratio between the aquifer and the drain (H_A/H_D) was then set by adjusting the constant head reservoir to a predetermined position. The appropriate drain or drains were then opened and the medium was allowed to drain to steady state, as indicated by constant water levels in all manometers and by a water balance between the input (Q_R) and measured output from both the drain (Q_D) and the aquifer (Q_A). Generally, steady state was achieved within 3 hours of the start of a test.

Results

In landfills, the success of a tile drain system for prevention of groundwater contamination can be described by the proportion of recharge that bypasses the tiles and reaches an underlying aquifer or deeper groundwater zone.

In the model, drain performance was measured as Q_A/Q_R where Q_A is the discharge from the lower aquifer. This describes both leakage past the drain and capture since at steady state $Q_A = Q_R - Q_D$, provided there is no contribution from the lower aquifer. For most cases Q_A/Q_R is positive, however for some combinations of $H_A/H_D > 1$ and low rainfall intensifies the lower aquifer began to discharge into the overlying sand. For these cases $Q_D > Q_R$ and drain performance is measured as $-Q_A/Q_R$. Figures 3 through 7 show the drain performance for a particular drain position and spacing (H_D/L), for varying rates of rainfall made dimensionless by using the ratio R/K_s.

Drain performance is clearly sensitive to all the variables examined in this study - R/K, H_A/H_D and H_D/L.



<ins>Figure 3</ins>: Drain performance versus rainfall intensity, $H_D/L = 0.32$.

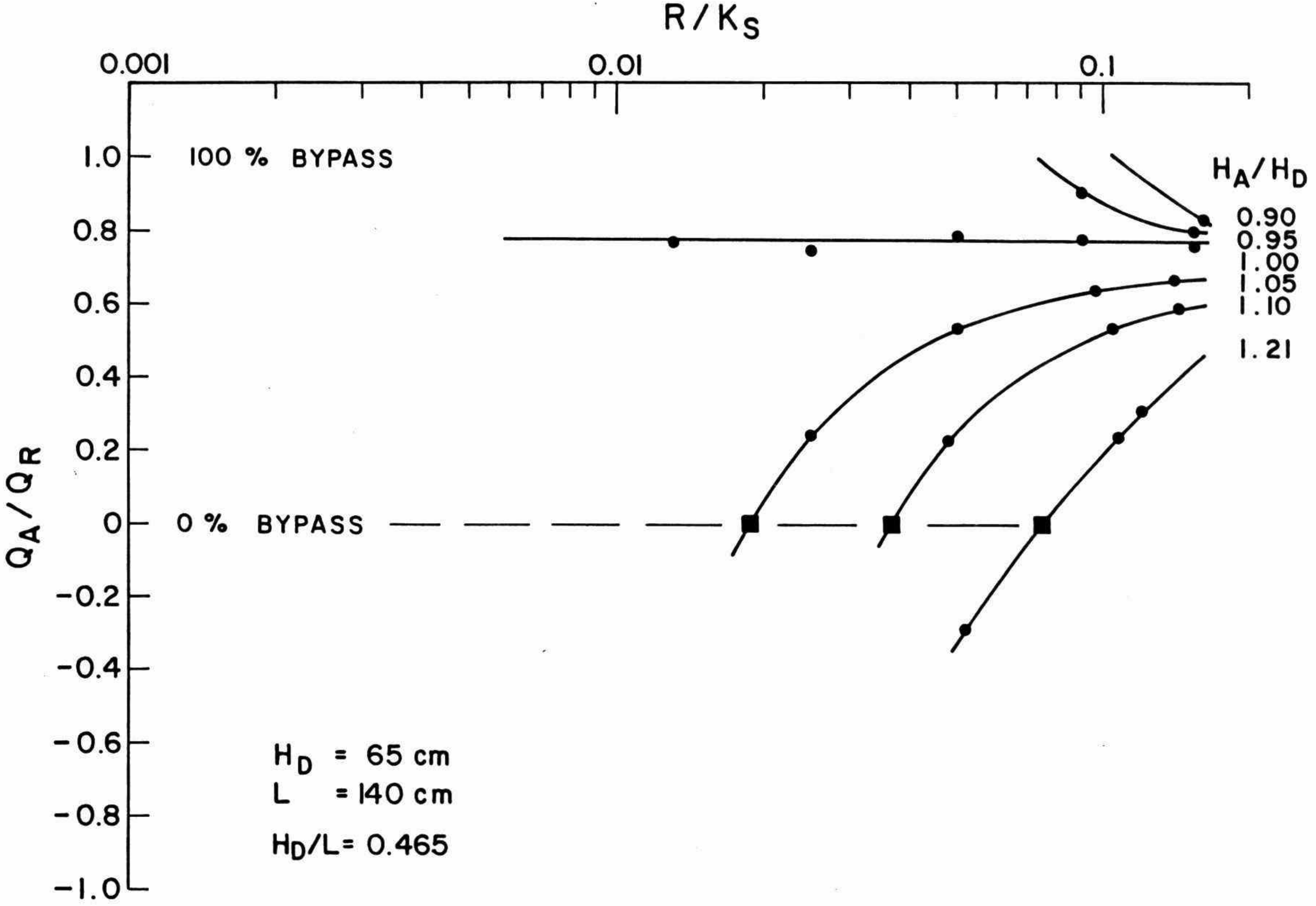


Figure 4: Drain performance versus rainfall intensity, $H_D/L = 0.465$.

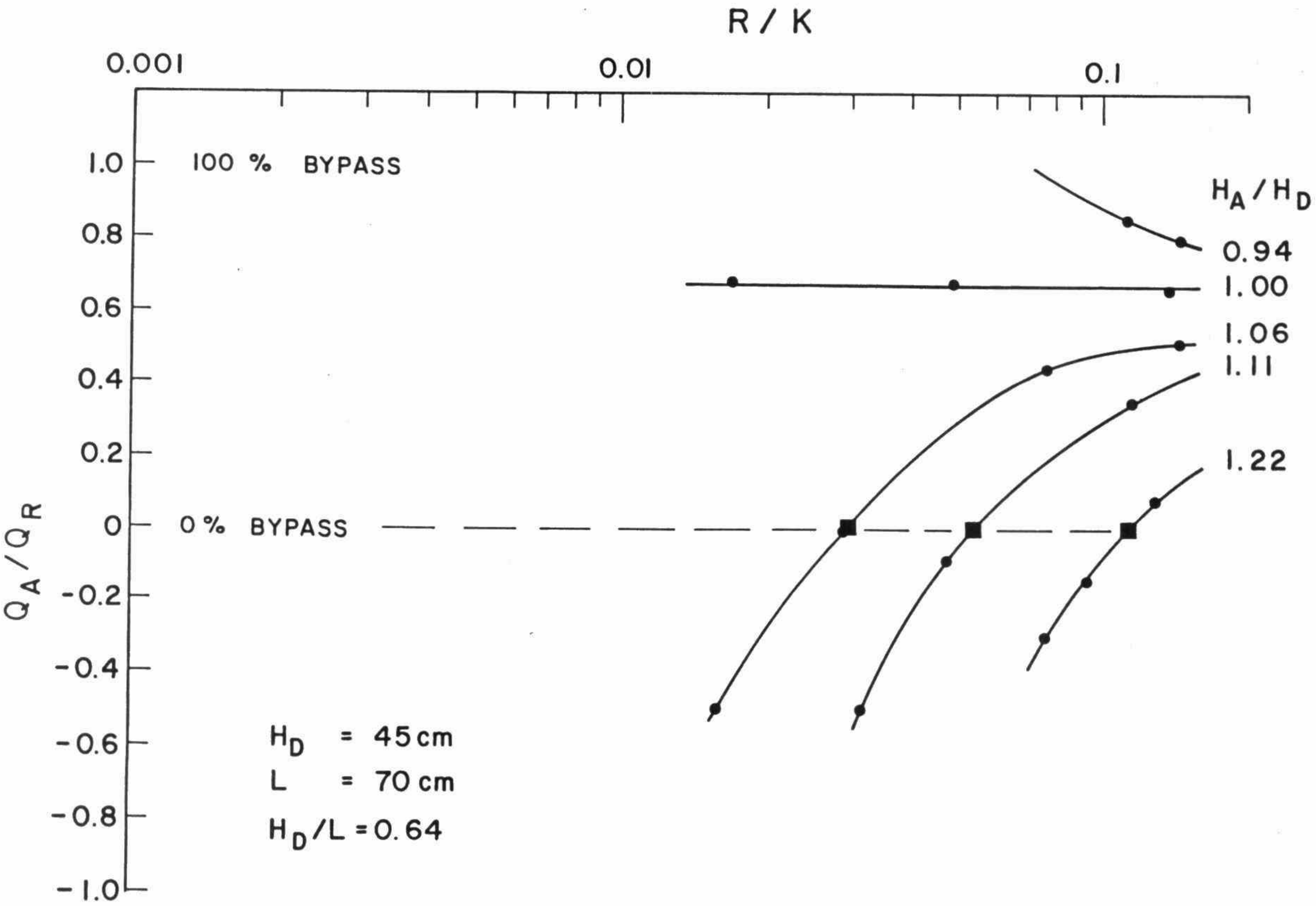


Figure 5: Drain performance versus rainfall intensity, $H_D/L = 0.64$.

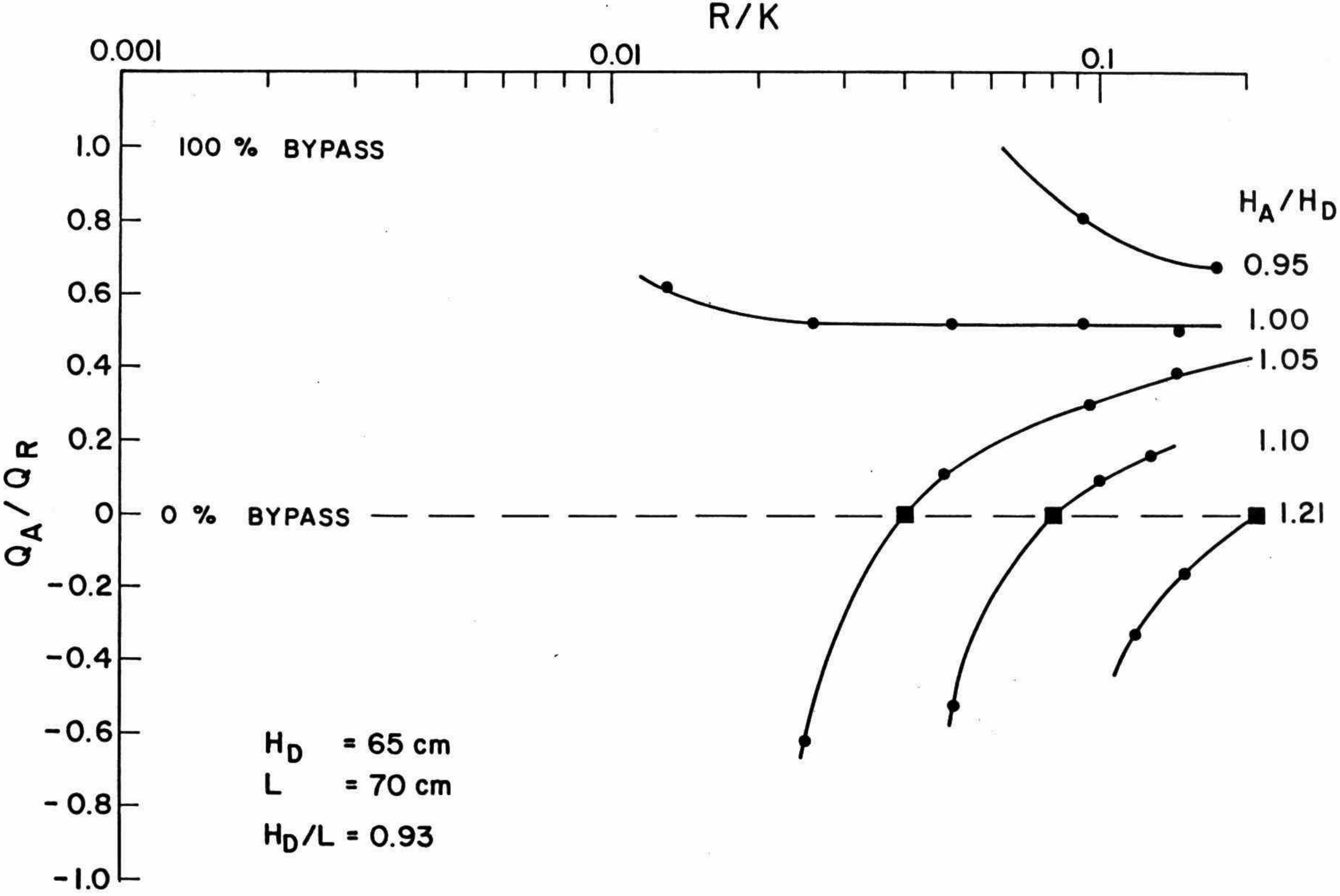


Figure 6: Drain performance versus rainfall intensity, $H_D/L = 0.93$

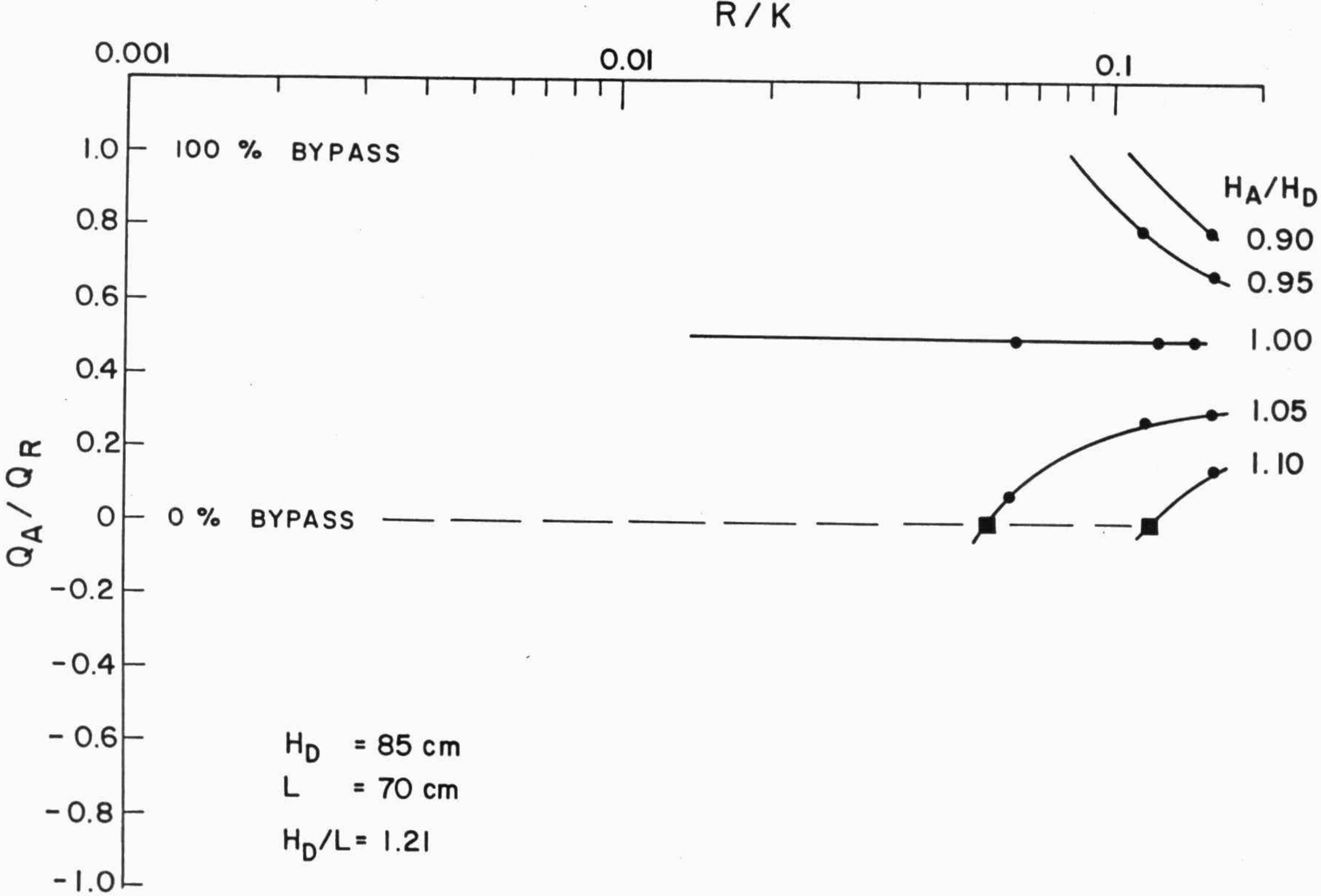


Figure 7: Drain performance versus rainfall intensity, $H_D/L = 1.21$.

Sensitivity to aquifer-drain head ratio (H_A/H_D)

The lower aquifer was included as part of the sand-box model to provide an opportunity for drainage through the bottom: otherwise all drainage of applied rainfall and infiltration would be forced to the "tiles" and collection would appear to be perfect for all tests. The aquifer was also a means of providing a nearly constant head across the bottom of the sand medium and served as the means of controlling vertical gradients to simulate field conditions of recharge and discharge zones. It is assumed that a permeability contrast of two orders of magnitude between the upper unit and basal aquifer is sufficient to justify conditions of constant head at depth during the recharge event.

It is clear from figure 3 through figure 7 that the head ratio (H_A/H_D) is a critical factor for the conditions tested. If the overall vertical gradient is downward at the tile ($H_A/H_D < 1$) then for the conditions tested in these experiments no more than 50% of the recharge from rainfall will be intercepted by the tiles. Figure 8 suggests that $H_A/H_D = 1$ is the lower limit for 100% collection although the extrapolations and generalizations shown may not be warranted from the available experimental results. However, these conditions can be tested further with the numerical model, beyond the physical limitations of the laboratory experiments. The influence of vertical gradients on drain performance is further illustrated in figures 9(a) and 9(b). Figure 9(a) shows the flow field for a drain configuration under downward gradient conditions ($H_A/H_D = 0.95$) in which 19% of surface infiltration was collected and 81% allowed to bypass to the lower aquifer. For the same drain configuration and similar rainfall conditions, Figure 9(b) shows the flow field between drains under an upward gradient condition (H_A/H_D = 1.05) which yielded 90% collection and only 10% bypass.

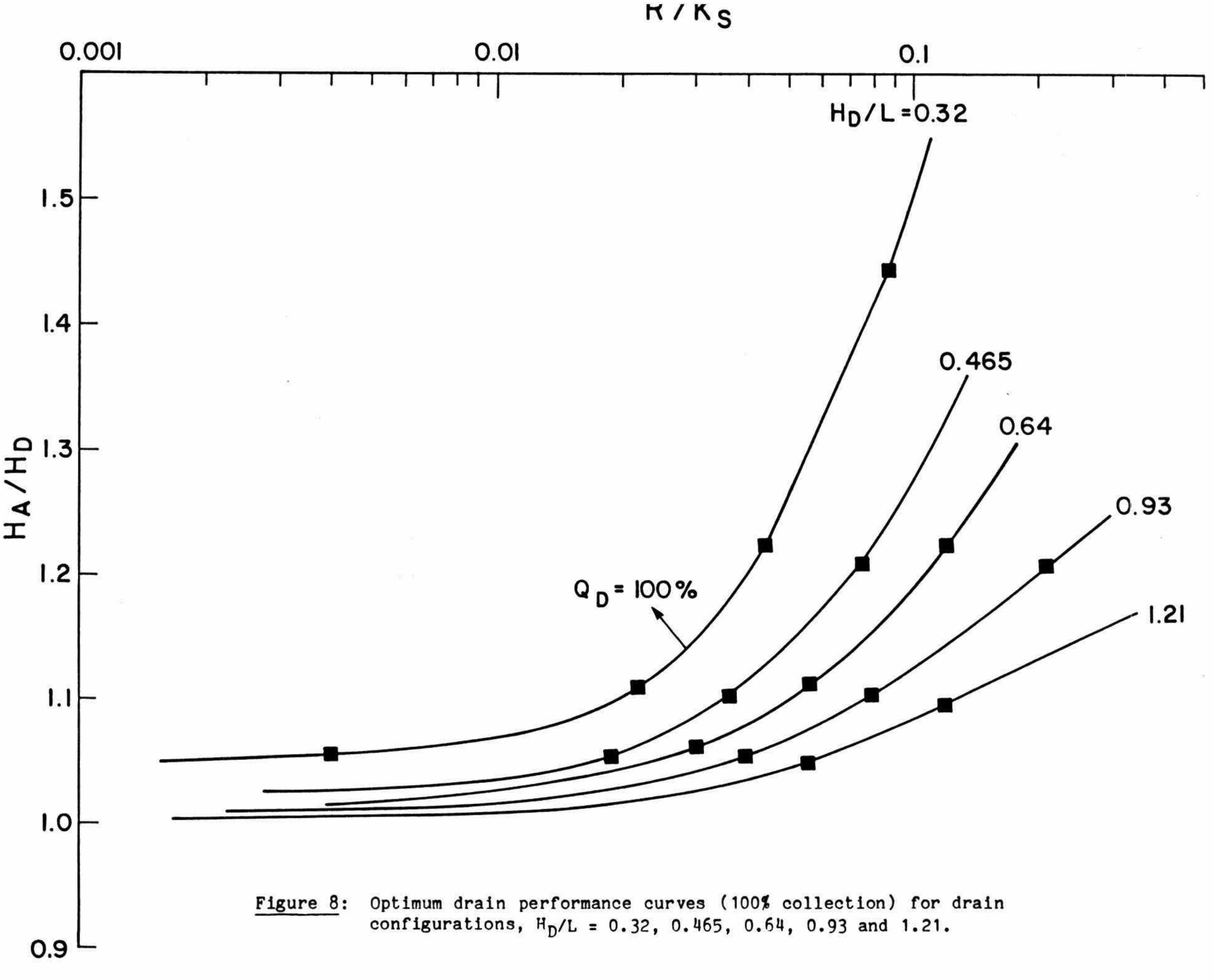


Figure 8: Optimum drain performance curves (100% collection) for drain configurations, H_D/L = 0.32, 0.465, 0.64, 0.93 and 1.21.

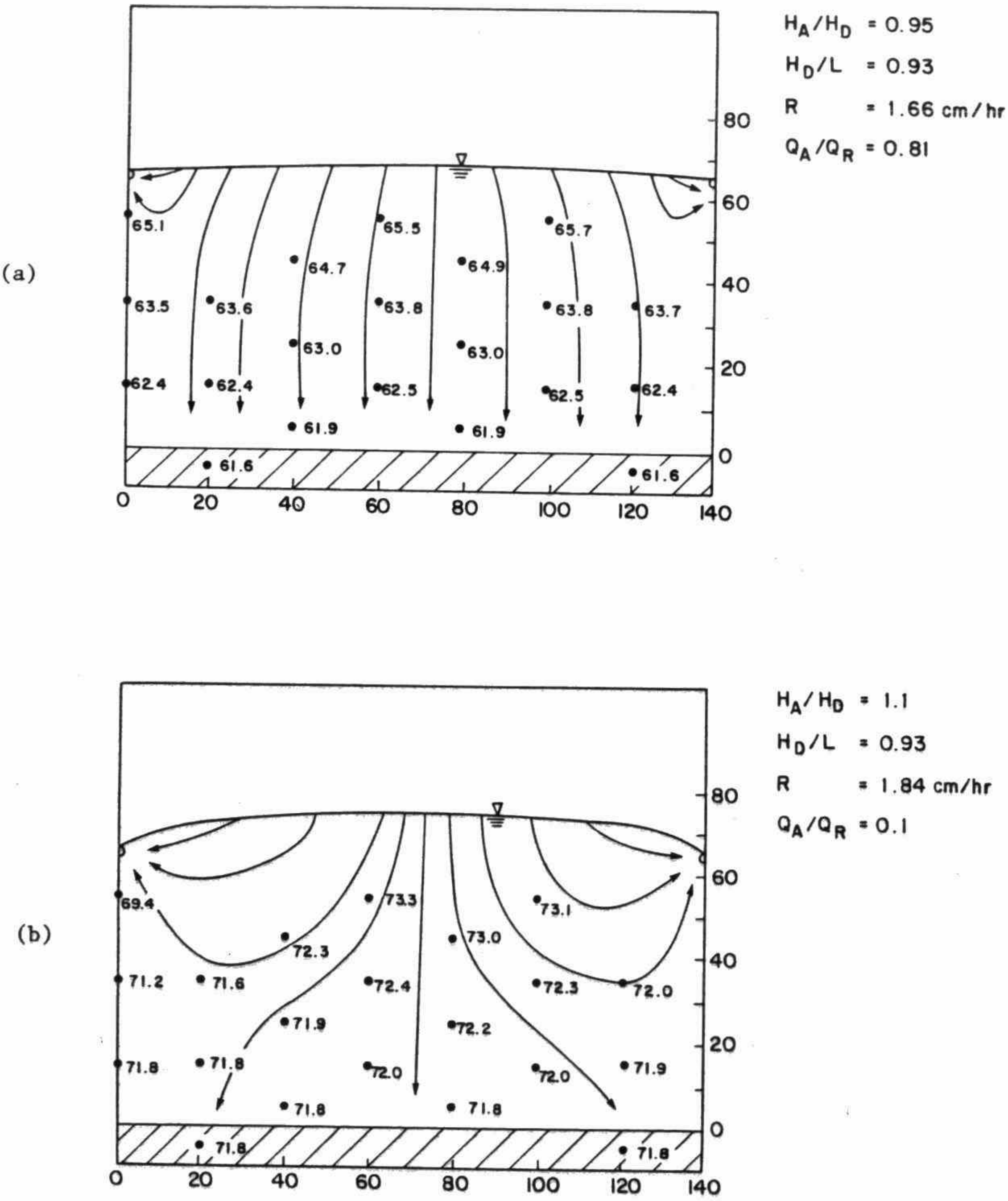
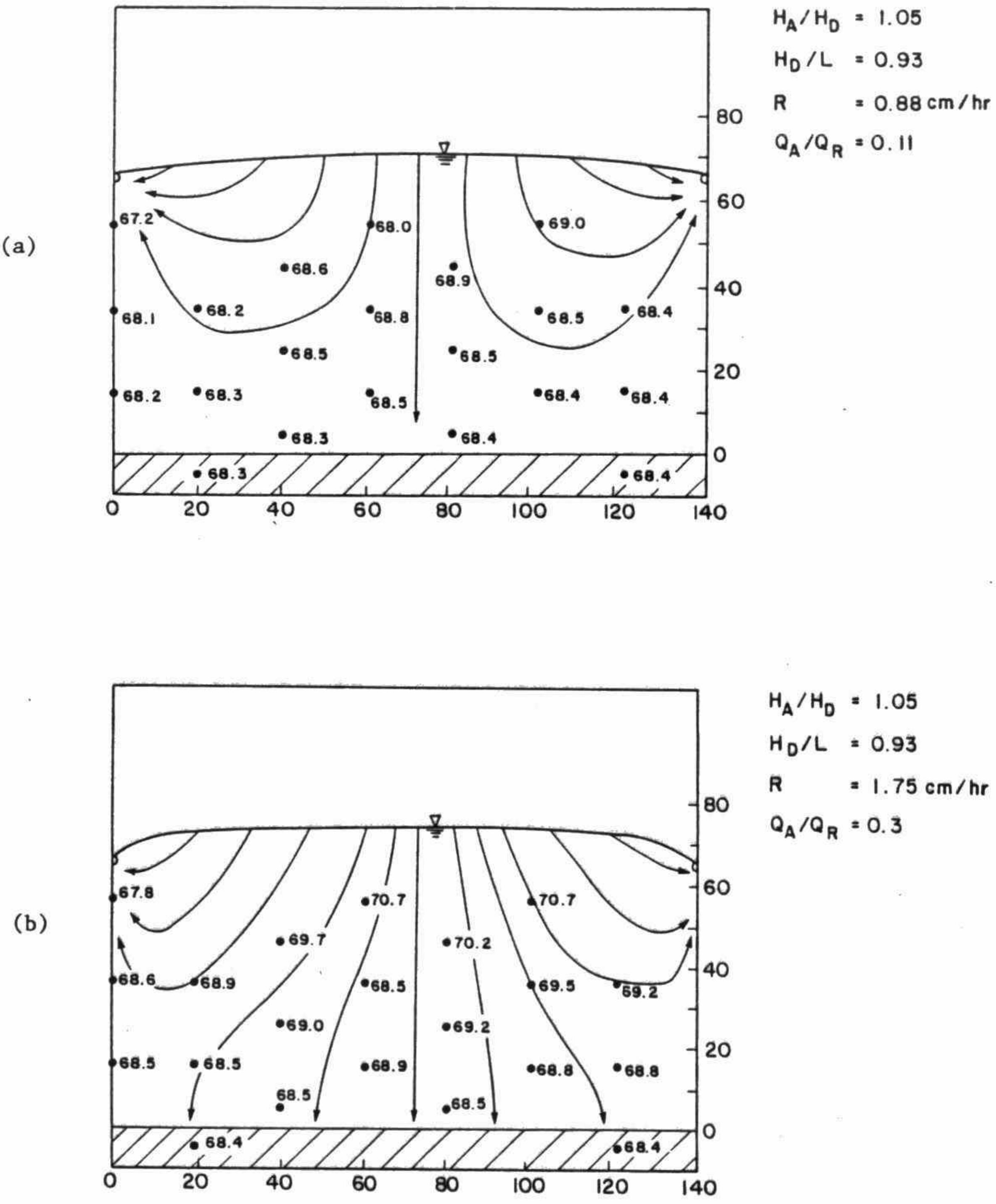


Figure 9: Hydraulic head distribution - sensitivity to hydraulic gradients (a) $H_A/H_D = 0.95$ (b) $H_A/H_D = 1.1$

Sensitivity to Rainfall Rate (R/K)

Figures 3 - 7 indicate an extreme sensitivity of drain performance to rainfall, for all conditions tested except $H_A/H_D = 1$. Where $H_A/H_D >$ 1, the performance declines (Q_A/Q_R increases) with increasing rainfall, because the higher rainfall causes a greater buildup of the groundwater mound between drains, and thus a greater head to drive water downward toward the aquifer. This condition is further illustrated through a comparison of figures 10(a) and 10(b) where a 20% increase in bypass was measured as the rainfall rate was doubled from 0.88 cm/hr to 1.75 cm/hr for $H_A/H_D = 1.05$ and $H_D/L = 0.93$.

Few tests were made for $H_A/H_D <$ 1 but it is clear that the generally poor performance improves as R/K_s increases. Where rainfall is low and the gradient is downward the groundwater mound between tiles is low so the effectiveness of the tile as a drain is reduced. For all curves of $H_A/H_D <$ 1 the point is reached where rainfall is so low that the water table stabilizes naturally below the tile drain, which then is not functional.



H_A/H_D = 1.05
H_D/L = 0.93
R = 0.88 cm/hr
Q_A/Q_R = 0.11

H_A/H_D = 1.05
H_D/L = 0.93
R = 1.75 cm/hr
Q_A/Q_R = 0.3

Figure 10: Hydraulic head distribution - sensitivity to rainfall intensity (a) R = 0.88 cm/hr (b) R = 1.75 cm/hr.

Sensitivity to Dimensions of the System H_D/L

The model indicates such poor performance for ($H_A/H_D < 1$) that this condition is not discussed here. For $H_A/H_D > 1$, the performance is more sensitive to H_D/L at low rainfall rates than higher rainfall rates. The influence of drain height (H_D) can be seen through a comparison of figures 3 and 4. For example figure 3 shows that for a given condition ($R/K_s = 0.02$, $H_A/H_D = 1.055$, L - 140 cm and $H_D = 45$ cm) $Q_A/Q_R = 0.48$, but Figure 4 shows for $H_D = 65$ cm, $Q_A/Q_R = 0.07$. For identical recharge rates and drain spacing, a drain placed in a landfill with a head ratio $H_A/H_D = 1.05$, will collect more leachate if it is higher above the aquifer than a drain in another landfill under the same $H_A/H_D = 1.05$ condition. A higher drain position increases the performance because the lower the drain, the greater the tendency for all flow lines to be directed downward and the greater the likelihood that they are diverted to the aquifer rather than the drain. The effect of drain spacing is evident in figures 11(a) and 11(b) where reducing the drain spacing by a factor of 2 corresponds to a 80% decrease in drain bypass ($Q_A/Q_R = 0.525$, $Q_A/Q_R = 0.11$) for identical conditions of H_A/H_D and R/K_s.

Figure 8 shows clearly the strong control exerted by H_A/H_D at low rainfall rates (R/K_s) and the strong influence of tile elevation and spacing at high infiltration rates. For low recharge rates (R/K_s) the groundwater mound between tiles is low and the upward gradient given by the head ratio (H_A/H_D) > 1 causes a general flow throughout the system toward the drain.

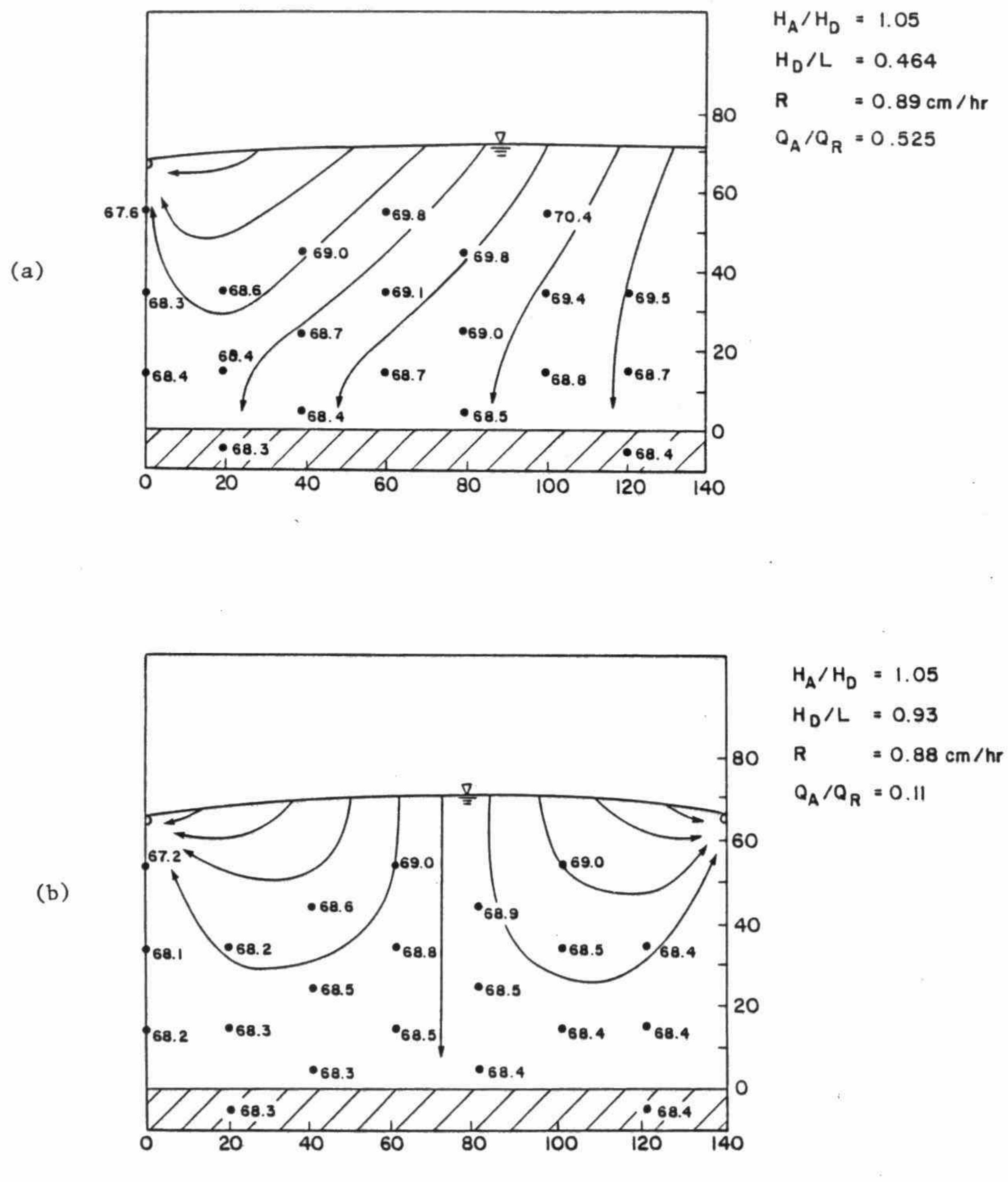


Figure 11: Hydraulic head distribution - sensitivity to drain configuration (a) $H_D/L = 0.464$ (b) $H_D/L = 0.93$

Discussion

Whenever model studies of idealized systems are applied to real field problems, some skepticism is raised, and warranted. The present study is no exception but it does show the sensitivity of a drains effectiveness to tile spacing and depth for some piezometric and recharge conditions. The isotropic and homogeneous medium is not encountered in the field but it represents the porous medium most favourable to downward flow, and therefore the most difficult to control. Any anisotropy due to grain orientation or stratification ($K_h/K_v > 1$) would favour horizontal flow toward the drain(s) and reduce leachate bypass to the aquifer.

The model had two layers but the lower sand "aquifer" served only to control head relations in the upper fine-grained sand medium, and to offer an opportunity for fluid to escape from the system. Thus the experimental results apply only to the upper sand - a single porous medium.

The head relations between the open drain(s) and the basal aquifer were set before each experiment but the gradients in the rest of the system could not be anticipated because the final, stable, position of the water-table was not predicted - it was a consequence of the interaction of all the factors of the system. However, the head relations in the model were set for each experiment to represent a condition that might be encountered in the field. Moreover, they were conditions that can be easily determined in the field and specified in design criteria as site characteristics. On the other hand, the final stable position of the water table in a landfill, with or without a tile-drain system, is a matter of performance of the final system as constructed and any prediction of the water table is subject to many uncertainties. Therefore, we think it is an advantage that the position of the water table is not a factor in our method of analysis.

Conclusions

In Ontario most proposed landfill sites are on materials of very low- to moderately low permeability. If the groundwater potential field below a site can be determined from piezometers, then a tile underlain system can be designed to collect almost all the leachate that may percolate from the wastes.

It is obvious that the spacing between tile drains is one important factor - the closer the spacing, the more effective the system. The depth of the tiles, or rather elevation of the tiles with respect to the hydraulic head at depth is another important factor. For many situations leachate will bypass the tile collection system if the tiles are either too deep or too shallow.

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DEVELOPMENT OF DESIGN CRITERIA FOR OPTIMAL RECOVERY OF LEACHATE UNDER SANITARY LANDFILLS

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Key words: Leachate, Leachate Recovery, Sanitary Landfills, Landfill Design.

ABSTRACT

This study proposes a numerical approach to evaluate the efficiency of leachate collection systems under landfills. It applies a finite element model to a 2-D steady-state flow system of variable hydraulic parameters and spatial dimensions.

Results for homogeneous, isotropic media show that most leachate can be collected if an upward gradient exists between the drain level and the bottom of the system. If the gradient is downward, the drains have to be closely spaced in order to collect the leachate. Drain performance depends also on the rate of recharge to the system which controls, in part, the height of the groundwater mound between tiles. Optimum recovery is attained when all leachate is collected with minimum infiltration from regional aquifer water. Further results show that natural and artificial anisotropy or layering in the porous medium can increase significantly the performance of a given design. Consequently, the presence of such characteristics can be a determining factor in the creation of efficient leachate recovery systems.

INTRODUCTION

A common problem with sanitary landfills is the uncontrolled migration of leachate beyond the landfill property. Engineered landfills are designed to contain the leachate within fixed boundaries. Some utilize tile drains placed at the bottom of the landfill to function as interceptors of the downward migrating leachate (Fig. 1). Regulations may require that the tile drains collect some specified percent of the leachate but very little is known about performance of tiles in this regard.

Tile drains have been used extensively for the drainage of agricultural land and their performance in this capacity has been the subject of extensive research. In these studies, the main concern is the lowering of the water table and its final configuration. If an impermeable base is assumed then all infiltration below the root zone will be diverted to the tiles; if an impermeable base is not assumed then some of the infiltrated water may bypass the collection system, but this is not a factor in performance for common agricultural applications.

Where tile drains are used in landfills to collect leachate, it is assumed that all infiltration that passes through the cover will become leachate. The main concern is to ensure that some specified portion of this will be collected and only the remainder will escape as contaminated groundwater. Thus, it is good practice to minimize infiltration by proper design and use of materials to reduce the amount of leachate that must be collected, handled and treated. The final position of the water table is not of primary importance in this use of tile drains.

In analyses of tile drainage of agricultural lands, normally only the upper

1-3 meters of the subsurface are of interest, so details of the lower boundary are of secondary importance. Groundwater flow under a landfill deals with deeper physical regions and so may be influenced by complex hydrogeologic conditions which must be dealt with in the analysis of pollution hazards. Approaches include analytical solutions, numerical models, laboratory experiments, and the use of electric and hydraulic models, usually for idealized flow systems.

Generally, the results of research on tile drains for agriculture indicate that:

a) the maximum height of the water table above the level of the tiles increases as the ratio of rainfall rate to saturated hydraulic conductivity increases: (Childs, 1943; Collis-George and Youngs, 1958; List, 1964; Youngs, 1974 and 1975);

b) the maximum height of the water table increases as the depth to the impermeable base decreases to a critical value beyond which the two are independent (Childs, 1943; Collis-George and Youngs, 1958; List, 1964; Youngs, 1975);

c) the maximum height of the water-table increases as the distance between tiles increases (Childs, 1943; Kirkham and De Zeuw, 1952; List, 1964); and

d) the maximum height of the water table is sensitive to the tile diameter and the spacing of gaps in the tile line. (Childs, 1943; Engelund, 1951; List, 1964; Sneyd and Hosking, 1976; Youngs, 1973).

The parameters considered in these investigations determine the configuration of the water table and therefore the pattern of groundwater flow. Nevertheless, we did not use the approach adopted in many of these studies because we wanted to base our analysis on parameters that could easily be determined in the field, rather than depending on a prediction of the final position of the water table which would merely add another step to the process and not in itself offer a clear indication of whether leachate would or would not escape from a particular landfill site. Further, we could not use an impermeable boundary (except at depth) in any of our analyses because that would preclude any escape of leachate from the model. Also, in our study, drainage was not enhanced by any means such as low permeability liners placed at the bottom of the landfill. Those cases have been investigated analytically by several authors including Wong (1977), Moore (1980), and MacBean et.al. (1982), and Dematrocopoulis et.al. (1984).

Most of the limitations of analytical methods can be avoided if the flow equation is solved by numerical methods. In particular, Pickens, et al., (1979) showed the potential usefulness of a finite element numerical model in a study of migration of pesticides toward tile drains.

The specific objective of this study is to use numerical simulations and a two-dimensional finite-element flow model to determine the relationship between some of the parameters governing the flow of fluid towards tile drains in a homogeneous isotropic medium. This study is limited to a consideration of uniform recharge and steady-state flow in a uniform unconfined aquifer. Transient flow conditions will be dealt with in later studies.

THE MODEL

The problem of steady-state flow to a tile drain can be most conveniently analyzed by using the dual theory of flow which combines potential functions and streamfunctions into one unified model. This well-established and useful theory is, unfortunately, little known at present in hydrogeologic circles and for this reason Frind and Matanga (1985) produced a concise review in a form that is meaningful to the practical hydrogeologist.

The advantages of the dual approach, compared with the conventional approach based on potential theory only, is that flownets are produced directly rather than by laborious interpolation of velocity vectors or by graphical procedures. The accurate flownets that are produced can be used for the calculation of discharges and the simple visual determination of advective transport of contaminants. They also facilitate the calculation of travel times or travel distances in flow systems of irregular geometry.

The theory is based on the existence of a potential function $\phi = \phi\ (x,y)$ and a streamfunction $\psi = \psi\ (x,y)$ for the case of a two-dimensional x,y coordinate system. The specific discharge (Darcy discharge) vector $\underset{\sim}{q}$ can be expressed in general form as

$$\left\{\begin{matrix} q_x \\ q_y \end{matrix}\right\} = -\begin{bmatrix} K_{xx} & K_{xy} \\ K_{yx} & K_{yy} \end{bmatrix} \left\{\begin{matrix} \frac{\partial\phi}{\partial x} \\ \frac{\partial\phi}{\partial y} \end{matrix}\right\} = \left\{\begin{matrix} \frac{\partial\psi}{\partial y} \\ -\frac{\partial\psi}{\partial x} \end{matrix}\right\} \qquad (1)$$

where K_{ij} is the hydraulic conductivity tensor. Equation (1) thus relates the discharge $\underset{\sim}{q}$ to both ϕ and Ψ. For the case where the coordinate axes coincide with the principal directions of permeability, equation (1) simplifies to:

$$\left\{\begin{matrix} q_x \\ q_y \end{matrix}\right\} = -\left\{\begin{matrix} K_{xx}\frac{\partial\phi}{\partial x} \\ K_{yy}\frac{\partial\phi}{\partial y} \end{matrix}\right\} = \left\{\begin{matrix} \frac{\partial\psi}{\partial y} \\ -\frac{\partial\psi}{\partial x} \end{matrix}\right\} \qquad (2)$$

where K_{xx} and K_{yy} are the principal components of K_{ij}.

The dual continuity equations in principal direction form are

$$\frac{\partial}{\partial x}\left(K_{xx}\frac{\partial\phi}{\partial x}\right) + \frac{\partial}{\partial y}\left(K_{yy}\frac{\partial\phi}{\partial y}\right) = 0 \tag{3a}$$

$$\frac{\partial}{\partial x}\left(\frac{1}{K_{yy}}\frac{\partial\psi}{\partial x}\right) + \frac{\partial}{\partial y}\left(\frac{1}{K_{xx}}\frac{\partial\psi}{\partial y}\right) = 0 \tag{3b}$$

The boundary conditions are also expressed in dual form. For a boundary where the head is known (for example a watertable boundary), the boundary conditions take the form:

$$\phi = \phi_0 \tag{4a}$$

and

$$\underset{\sim}{g}^{\psi} \cdot \underset{\sim}{n} = -\nabla\phi \cdot \underset{\sim}{r} \tag{4b}$$

where n is the unit normal vector to the boundary, r is the corresponding tangential vector, and g is defined by

$$\begin{Bmatrix} g_x^{\psi} \\ g_y^{\psi} \end{Bmatrix} = \frac{1}{|K|}\begin{bmatrix} K_{xx} & K_{xy} \\ K_{yx} & K_{yy} \end{bmatrix}\begin{Bmatrix} \frac{\partial\psi}{\partial x} \\ \frac{\partial\psi}{\partial y} \end{Bmatrix} = \begin{Bmatrix} \frac{\partial\phi}{\partial y} \\ -\frac{\partial\phi}{\partial x} \end{Bmatrix} \tag{5}$$

Thus a known head ϕ_0 enters the potential equation directly in the form of a first-type boundary condition, and the streamfunction equation indirectly in the form of a second-type boundary condition expressed in terms of the (negative) rate of change of the head along the boundary.

For a boundary where the flux is known, the boundary conditions take the form:

$$\underset{\sim}{g}^{\phi} \cdot \underset{\sim}{n} = (\underset{\approx}{K}\nabla\phi) \cdot \underset{\sim}{n} \tag{6a}$$

and

$$\psi(\Gamma) = \psi_0(\Gamma_0) + \int_{\Gamma_0}^{\Gamma} \underset{\sim}{q}_0 \cdot \underset{\approx}{n}\, d\Gamma \tag{6b}$$

where Γ represents the boundary. The specified flux q_o enters the potential equation in the form of a second-type boundary condition and the streamfunction equation in the form of a first-type boundary condition by integration of the flux along the boundary. In the special case of an impermeable boundary (or a symmetry boundary), the normal flux is zero and the boundary is a streamline.

Figure 1 represents a simple, hypothetical situation, selected for consideration in this study because it matches a physical model being used in the experimental phase of this research project (See RAC 153 PL First Year Report). If the tiles shown on Figure 1 are placed equidistant along a horizontal plane, then flow will be symmetrical about any interior tile and also about the midpoint between two tiles. The solution to the flow field can then be simplified by considering only a half-cell, with appropriate boundary conditions, rather than the entire region under the landfill. Figure 2 shows the cell with boundary conditions and table 1 shows the symbols used in this paper. Regional flow and conditions external to the half-cell are not considered in this paper. Since it is desired to study a homogeneous system, it is necessary to assume that the hydraulic conductivity for the landfill is the same as the hydraulic conductivity of the underlying porous medium.

The bottom boundary of the cell (taken as datum elevation) is assumed to adjoin a hydrogeologic unit having much greater hydraulic conductivity than the cell itself (Fig. 1). The head at the bottom boundary can, therefore, be taken as constant. Other conditions at depth will be investigated later.

The physical parameters of the half-cell system are the hydraulic conductivity K, the recharge R, the length L, and the heads H_A and H_D at the bottom boundary and the drain respectively. (See Fig. 2 and Table 1 for further definitions). At the watertable boundary, the total recharge per unit width of the flow system (RxL) will be divided into an amount Q_D which will be captured by the drain, and an amount Q_A which will flow downward through the cell and enter the lower aquifer. In addition, there may also be an amount Q_I entering the cell from the lower aquifer.

The position of the watertable is not known a priori but depends on the recharge R. For each combination of parameters, the watertable position will be determined iteratively by the model.

The objective of the analysis will be to vary the parameters K, R, H_A, H_D, and L and to determine the resulting recharge/discharge quantities Q_D and Q_A The ratios of these discharges can be taken as a measure of the performance of the drain system.

The boundary conditions for the dual model can be defined by taking the bottom of the cell as the datum elevation, the watertable as a surface of zero pressure, and top left corner as the reference point for the streamfunctions. The drain itself is assumed to be part of the left symmetry boundary of the model. The boundary conditions for the potential model and the streamfunction model are as follows:

Top left corner:

$\Psi = \Psi_o = 0$

Watertable (assuming slope of watertable is small).

$$q_o = R$$

$$\Psi = \Psi_o + \int_o^L R \; dx$$

Right boundary (center of cell):

$$q_x = 0$$

$$\Psi = RL$$

Bottom:

$$\phi = H_A$$

$$\frac{\partial \Psi}{\partial y} = 0$$

Left boundary (between bottom boundary and drain):

$$q_x = 0$$

$$\Psi = RL - Q_A + Q_I$$

Drain:

$$\phi = H_D$$

$$\int_{\text{drain}} q_x \, dy = - \int_{RL-Q_A+Q_I} d\Psi = Q_D$$

Left boundary (above drain):

$$q_x = 0$$

$$\Psi = 0$$

The flow region is discretized into triangular elements and a solution for ϕ

or Ψ at a finite number of nodal points is obtained by the Galerkin finite element technique. A comprehensive description of the solution method is given by Frind and Matanga (1985). The solution takes place in three steps, namely:

1. the solution of eqn. (3a) for heads ϕ ,
2. the determination of boundary fluxes on the basis of the calculated heads,
3. the solution of eqn. (3b) for streamfunctions Ψ . After the solution has been completed, the functions Φ and Ψ are contoured to produce a flownet.

It is during step 1 that the iterative scheme is used to determine the position of the watertable required to obtain a balanced steady-state flow system. In this scheme, the finite element grid is allowed to expand or contract so that the elevation of the upper boundary nodes matches the calculated hydraulic head at these nodes. Each iteration consists of a complete solution for head, followed by a comparison of the boundary heads to the elevation of the boundary nodes and a commensurate adjustment of the nodal elevations. Interior nodes situated above the level of the drain are also adjusted in order to keep element heights in proportion. The iterative procedure is completed when the difference between calculated head and elevation along the upper boundary falls within a predetermined tolerance or when the water table falls below the level of the drains or rises above the ground surface.

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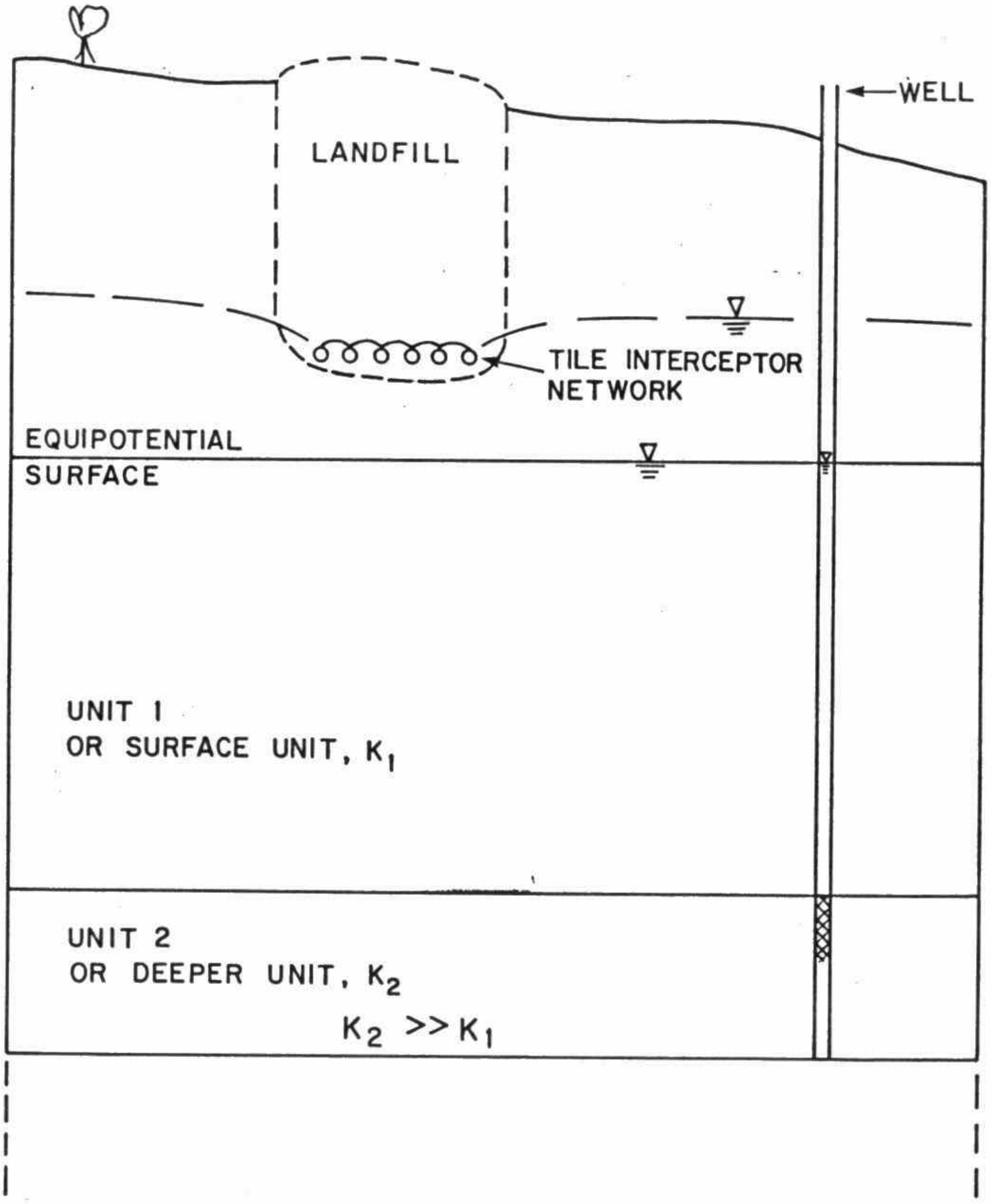

Figure 1. Schematic view of a hypothetical site.

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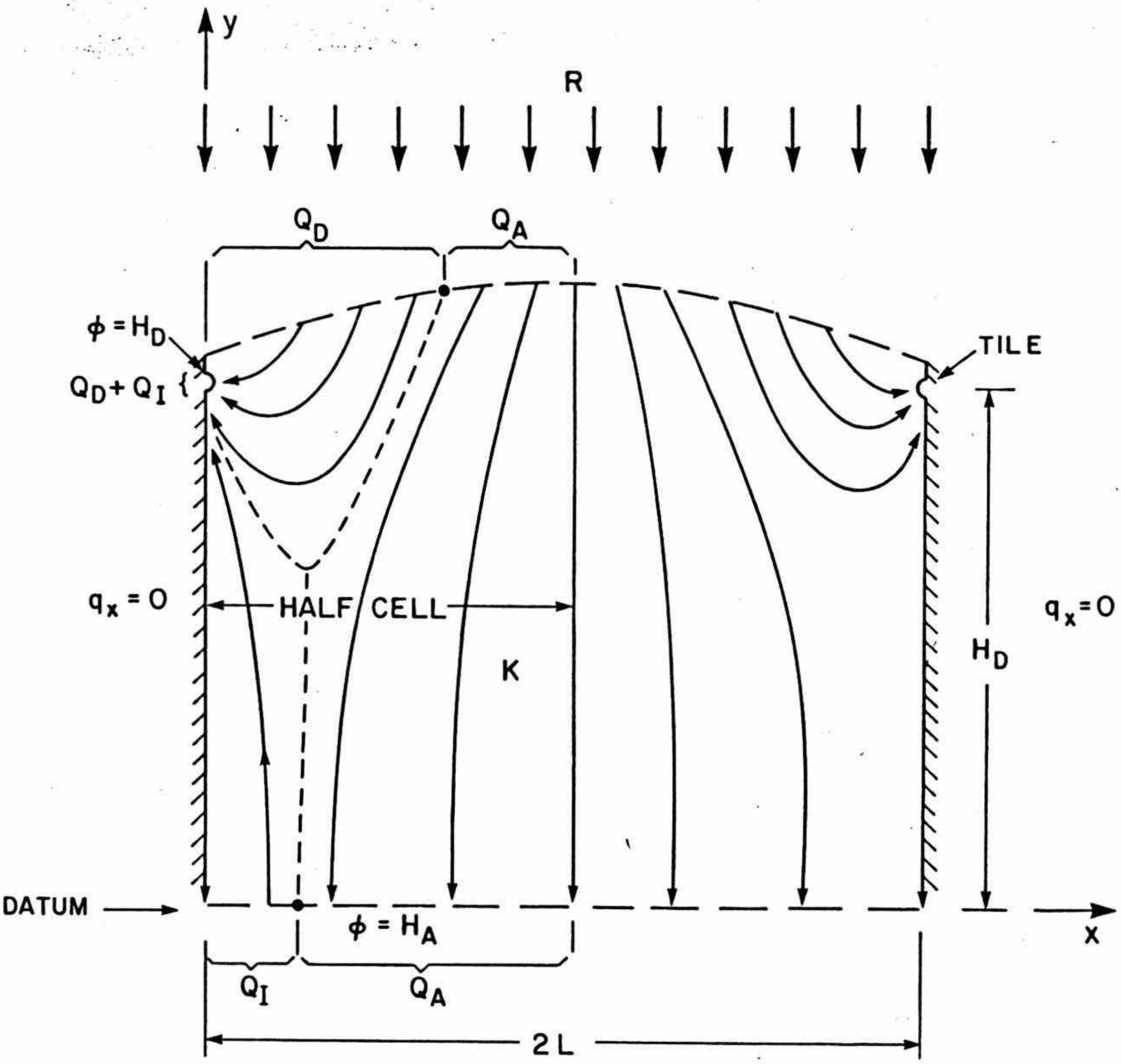

Figure 2. Drainage cell with boundary conditions and symbols.

VARIABLE	DESCRIPTION	UNITS
Q_A	Discharge of fluid leaving system through bottom per unit width of cell	L^2/T
Q_D	Discharge of fluid leaving system through drain per unit width of cell	L^2/T
Q_I	Recharge due to fluid entering system through bottom per unit width of cell	
H_A	Hydraulic head along the bottom of system.	L
H_D	Hydraulic head at drain.	L
L	Half spacing between drains.	L
R	Recharge flux.	L/T
K	Saturated hydraulic conductivity.	L/T
Q_A/Q_D	Drain performance factor, inversely proportional to drain efficiency.	-
R/K	Hydraulic condition factor.	-
H_A/H_D	Induced head ratio.	-
H_D/L	Cell geometry factor.	-

Table 1. Description of system variables.

SIMULATION RESULTS AND DISCUSSION

A total of 150 simulations were made. These simulations were designed to evaluate the sensitivity of Q_A/Q_D to H_A/H_D, R/K and H_D/L. Q_A represents the leachate which reaches the aquifer and, therefore, Q_A/Q_D is a measure of the hazard or inefficiency of the system[1]. H_A/H_D is the head ratio, which expresses the relationship between the hydraulic head at some selected depth and the drain elevation. Both head values are known or selected values. R/K is the ratio of recharge, or vertical flux, to the saturated hydraulic conductivity. Groundwater recharge is always difficult to evaluate with certainty, but for a given field situation the results show that reasonable estimates of the hydraulic conductivity of the medium place a considerable restriction on the likely range of the recharge, and thereby the ratio R/K. Uncertainty in values of Q_A/Q_D is estimated to be near 10%. Improvement in this figure is expected if a finer discretization is used. This will be done in further studies.

Q_A/Q_D versus R/K: $H_A/H_D = 1.0$

Figure 3 shows the results of 50 simulations plotted as log R/K versus log Q_A/Q_D, with the head ratio, H_A/H_D held constant at 1.0. Values of H_D of 20, 15 and 10 m were considered with different values of L to give ratios of H_D/L from 0.75 to 10.

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[1] In some cases it is more convenient to represent the performance of the system using the ratio Q_A/RL. This ratio was used in RAC 153 PL, "Laboratory Study of Tile Drain Efficiencies in Leachate Collection." Comparison between the results of the two approaches will be presented in the next report.

For all values of H_D/L, the relationship between R/K and Q_A/Q_D shows the same trend; Q_A/Q_D, the measure of the inefficiency of the system decreases by a factor of 2 as R/K increases over two orders of magnitude. At values of R/K less than 0.02, Q_A/Q_D is high and approaches a high constant value; at R/K values greater than 0.8, Q_A/Q_D is low and approaches a low constant value; for intermediate values of R/K the Q_A/Q_D changes uniformly. For all simulations with H_A/H_D = 1.0, recharge Q_I from the lower aquifer was zero.

The apparent limits of Q_A/Q_D at high and low R/K values can be related to the physical limits on the height of the groundwater mound produced. In general, as the recharge increases, the height of the mound increases. For high values of R/K, the ground surface imposes a constraint on the watertable rise, therefore, both Q_A and Q_D will tend to a constant limit. The lower limit of R is zero and the corresponding watertable will be horizontal (for the case when $H_A/H_D = 1$) producing no flow. Therefore, as $R \rightarrow 0$, either $Q_A/Q_D \rightarrow 0$ or $Q_A/Q_D \rightarrow \infty$, depending on which of Q_A or Q_D approaches zero faster. Which of the two limits is approached depends also on the ratio H_A/H_D; that aspect will be discussed in the next section.

Figure 4 shows the increase of the efficiency of the tile drain as the ratio H_D/L is increased. H_D might be considered the depth at which leachate is deemed to have bypassed the collection system and escaped to contaminate the groundwater reservoir. The value attributed to H_D will normally be obvious from hydrogeologic conditions at a site - for example, the position of the tile with respect to the depth of an aquifer or relatively permeable zone. In some circumstances it may be arbitrarily specified at a depth we can reasonably expect the head to be constant. The influence of H_D is perhaps not as obvious as that of tile spacing. Increasing the thickness of the medium and zone of interest below the level of the tile, leads to a lengthening of the vertical flow paths, and to maintain hydraulic gradients that are adequate to transmit the recharge, the water table rises and the slope on the water table increases. This relationship between the maximum height of the water table above the level of the tiles and the thickness of the flow zone, is opposite to that obtained from several drainage studies (including Childs, 1943; Collis-George and Youngs, 1958 and List, 1964) because in these cited studies it was assumed that the bottom of the aquifer was impermeable to flow and therefore, vertical flow through the medium was not a factor in water table slope nor in leachate bypass. Although the slope of the water table increases as H_D is increased, overall the vertical gradient decreases and discharge through the tiles increases.

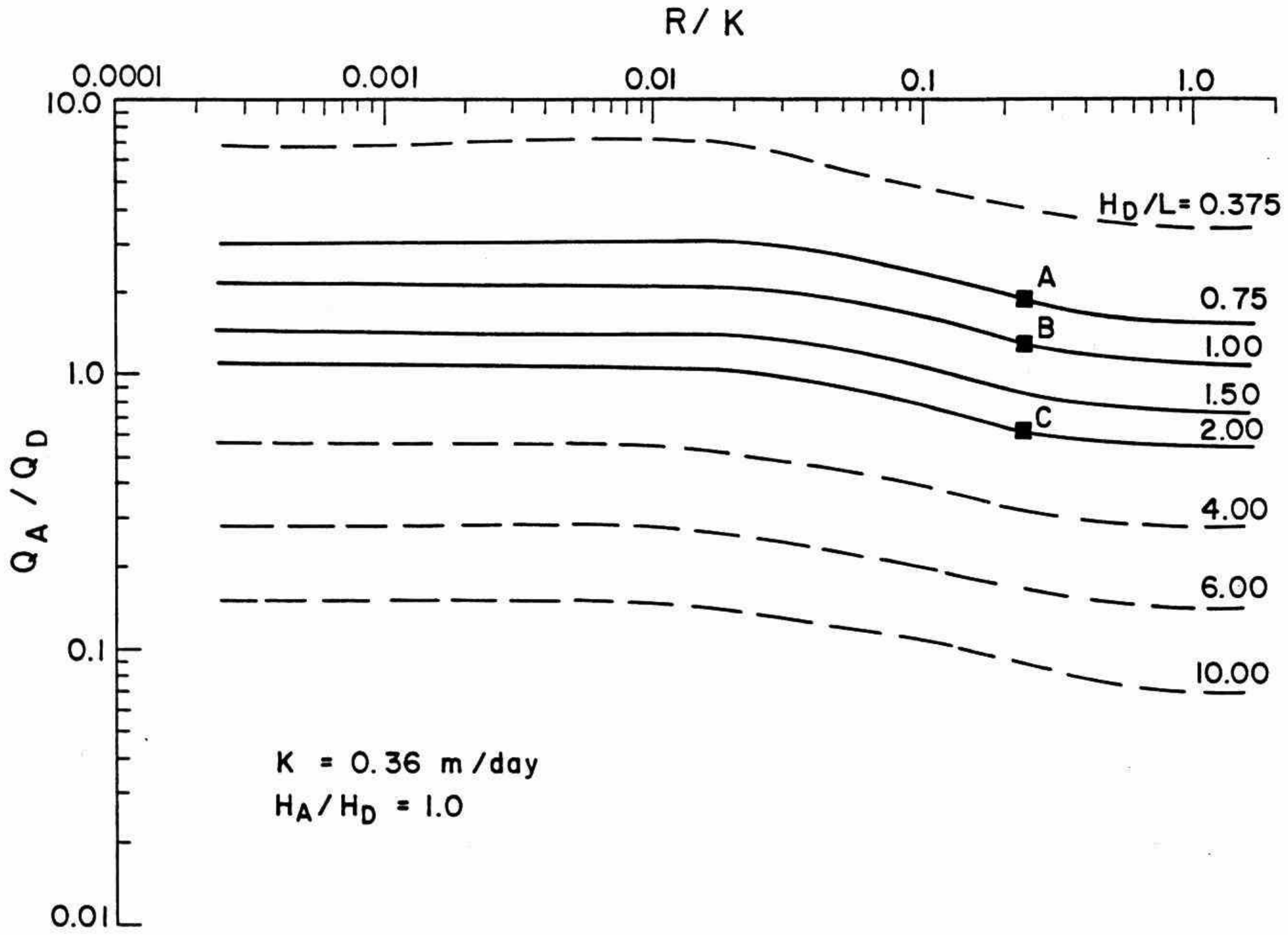
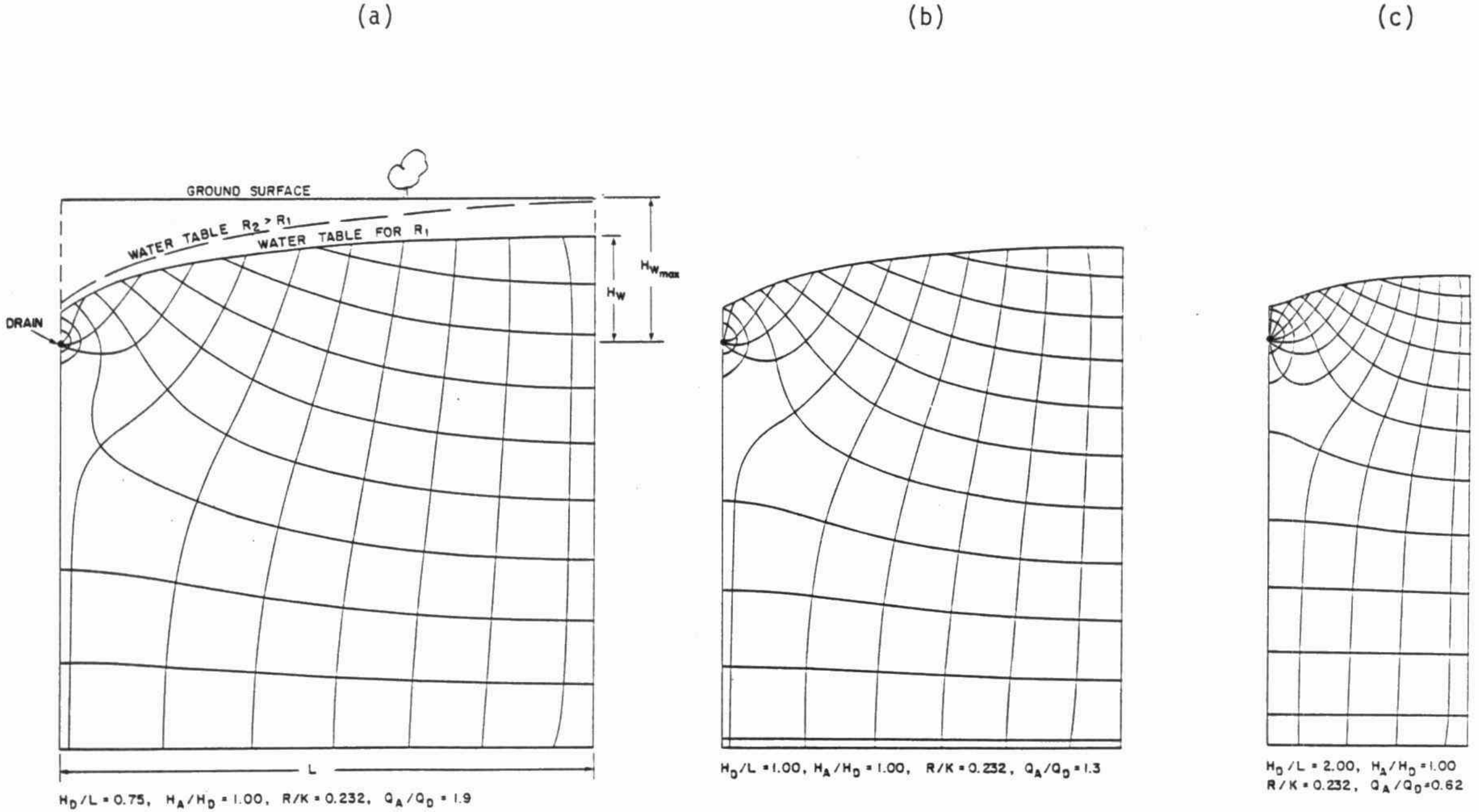


Figure 3. Graph showing drain efficiency (Q_A/Q_D) as a function of hydraulic conditions (R/K), in a case where no hydraulic gradient is induced between the bottom of the system and the drain (H_A/H_D is equal to 1.0.) The different curves correspond to different cell geometry factors (H_D/L).



$H_D/L = 0.75$, $H_A/H_D = 1.00$, $R/K = 0.232$, $Q_A/Q_D = 1.9$

$H_D/L = 1.00$, $H_A/H_D = 1.00$, $R/K = 0.232$, $Q_A/Q_D = 1.3$

$H_D/L = 2.00$, $H_A/H_D = 1.00$
$R/K = 0.232$, $Q_A/Q_D = 0.62$

Figure 4. Variations in resulting flow patterns with changes in the cell geometry factor (H_D/L). R/K and H_A/H_D are kept constant at 0.232 and 1.0 respectively. Cases a, b and c correspond to conditions A, B and C on figure 3.

Q_A/Q_D versus R/K: $0.8 \geq H_A/H_D \geq 1.2$

In Figure 5 the results of 75 simulations are plotted as R/K versus Q_A/Q_D on logarithmic graph paper. For these simulations H_D and L were arbitrarily held constant at 15 m and 20 m respectively, while values of H_A/H_D from 0.8-1.2 were tested.

Values of $H_A/H_D > 1$ represent the condition when the tiles are placed above the equipotential surface of the aquifer or zone of interest at depth. A downward gradient is present in the system. A typical flow pattern is shown on Figure 6A, which corresponds to conditions occurring at point D on Figure 5. It can be seen that most of the fluid is bypassing the drain; Q_A/Q_D has a value of 4.6.

Values of $H_A/H_D < 1$ represent the condition when the tiles are placed below the equipotential surface measured at depth, producing upward hydraulic gradients within the system. The relatively high head at depth greatly reduces downward flow. In the case of Fig. 6B, (point E on Fig. 5) Q_A/Q_D is equal to 0.96. It has to be remembered that the tile might also drain water from depth ($Q_I>0$) so the volume of fluid to be handled at the surface may be greater than the volume recharged over the landfill. Best drainage conditions are attained when a maximum amount of leachate and a minimum amount of water from depth are collected. Figure 6C (point F on Fig. 5) shows how these conditions are attained for the same geometry and head conditions as those of Figure 6B..

Figure 5 also indicates the limiting values of Q_A/Q_D referred to in the previous section. As the recharge approaches zero, the following occurs:

(a) $H_A/H_D<1$ (upward gradient):

$$\lim_{R \to 0} Q_A/Q_D = 0$$

(b) $H_A/H_D=1$ (zero gradient):

$$\lim_{R \to 0} Q_A/Q_D = \text{constant}$$

(c) $H_A/H_D>1$ (downward gradient):

$$\lim_{R \to 0} Q_A/Q_D = \infty$$

The value of Q_I is zero for all cases where H_A/H_D is larger or equal to 1. If H_A/H_D is smaller than 1, Q_I gets more important as H_A/H_D decreases. Therefore, if

$H_A/H_D<1$ (upward gradient)

$$\lim_{R \to 0} Q_I/Q_D = 1$$

This relationship is not apparent on Figure 5. A quantitative expression representing the importance of infiltration Q_I will be presented in a future report.

Comparison between Figures 3 and 5 shows what could be expected if a change in cell geometry occurs in cases of upward or downward induced hydraulic gradients. If H_D/L, the cell geometry factor, becomes larger, the performance of the drain increases and the whole set of curves of Figure 5 will move to the left. If H_D/L becomes smaller, the curves will move to the right of the graph, signifying poorer collection.

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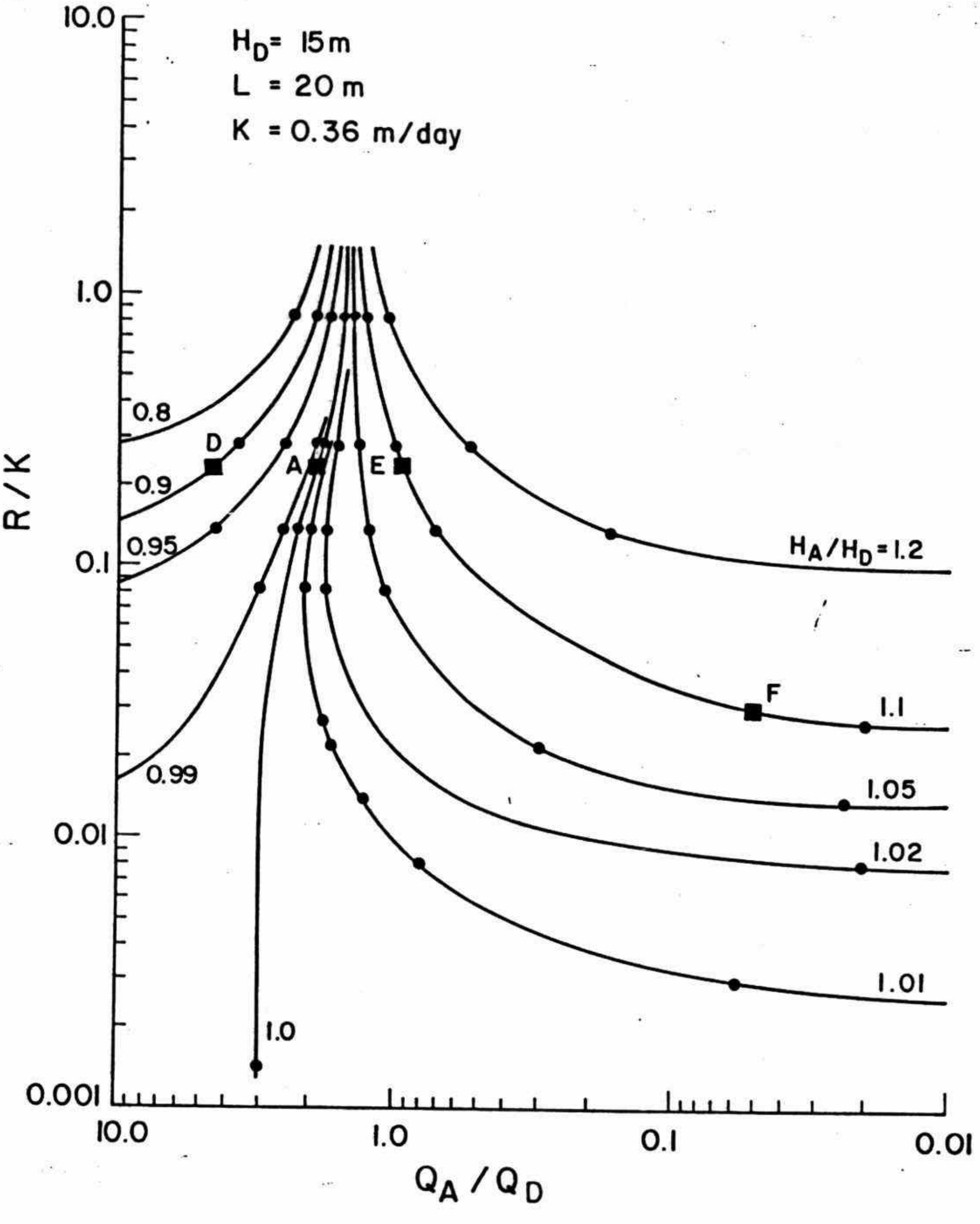

Figure 5. Graph showing drain efficiency (Q_A/Q_D) as a function of hydraulic conditions (R/K), in a case where vertical hydraulic gradients are present in the cell after positioning of the tile drain. Different curves represent different values of ratio H_A/H_D. Cell geometry factor (H_D/L) is equal to 0.75.

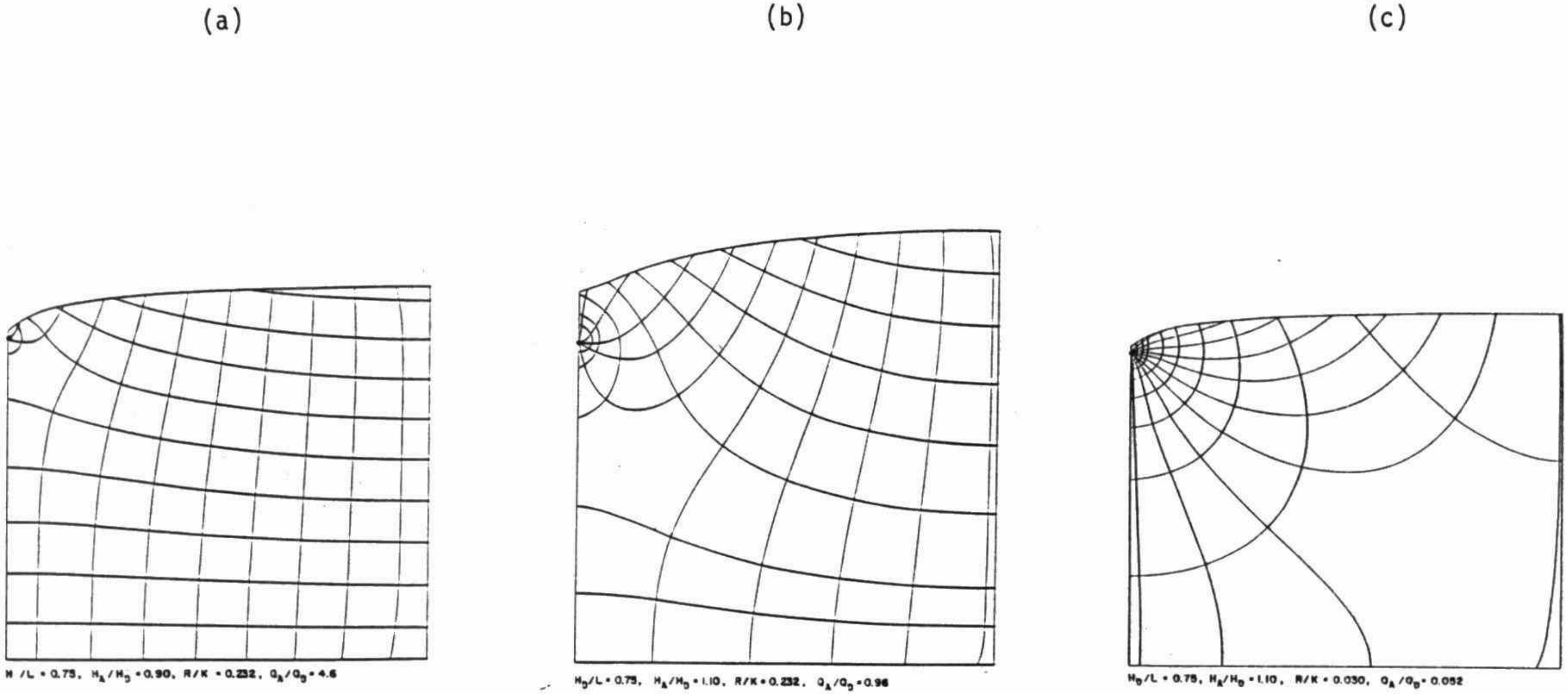
(a)
(b)
(c)
$H/L = 0.75$, $H_A/H_D = 0.90$, $R/K = 0.232$, $Q_A/Q_D = 4.6$
$H_D/L = 0.75$, $H_A/H_D = 1.10$, $R/K = 0.232$, $Q_A/Q_D = 0.96$
$H_D/L = 0.75$, $H_A/H_D = 1.10$, $R/K = 0.030$, $Q_A/Q_D = 0.052$

Figure 6. Variations in flow patterns with changes in induced gradient ratio (H_A/H_D) and hydraulic conditions (R/K). Cases a, b and c correspond to conditions D, E and F on figure 5.

Q_A/Q_D versus L and H_D

The results of 24 simulations are presented in Figure 7 as log L and log H_D versus log Q_A/Q_D. In both sets of plots, the relationship between the pairs of parameters is best described by a straight line.

Consistent with Figure 3, the results in Figure 7 show that Q_A/Q_D increases as L increases. In particular, the slope of the straight line between log L and log Q_A/Q_D is the same for the following combination of parameters:

$R/K > 0.02$ $H_A/H_D = 1$
< 1.00 $= 1, 1.1, 0.9$
$= 0.10$ $= 1$

Included in Figure 7 are plots of log H_D versus log Q_A/Q_D for three sets of R/K values, H_D and H_A/H_D being held constant. These results indicate that, unlike the L versus Q_A/Q_D relationship, log Q_A/Q_D decreases linearly as log H_D increases. Again, the straight line relationship between log H_D and log Q_A/Q_D has the same slope for the combination of values of R/K and H_A/H_D used in the simulations. If the slope of this straight line is known, only one coordinate point is required to construct the relationship between log H_D and log Q_A/Q_D for a set of values of R/K, H_A/H_D and L within the specified range.

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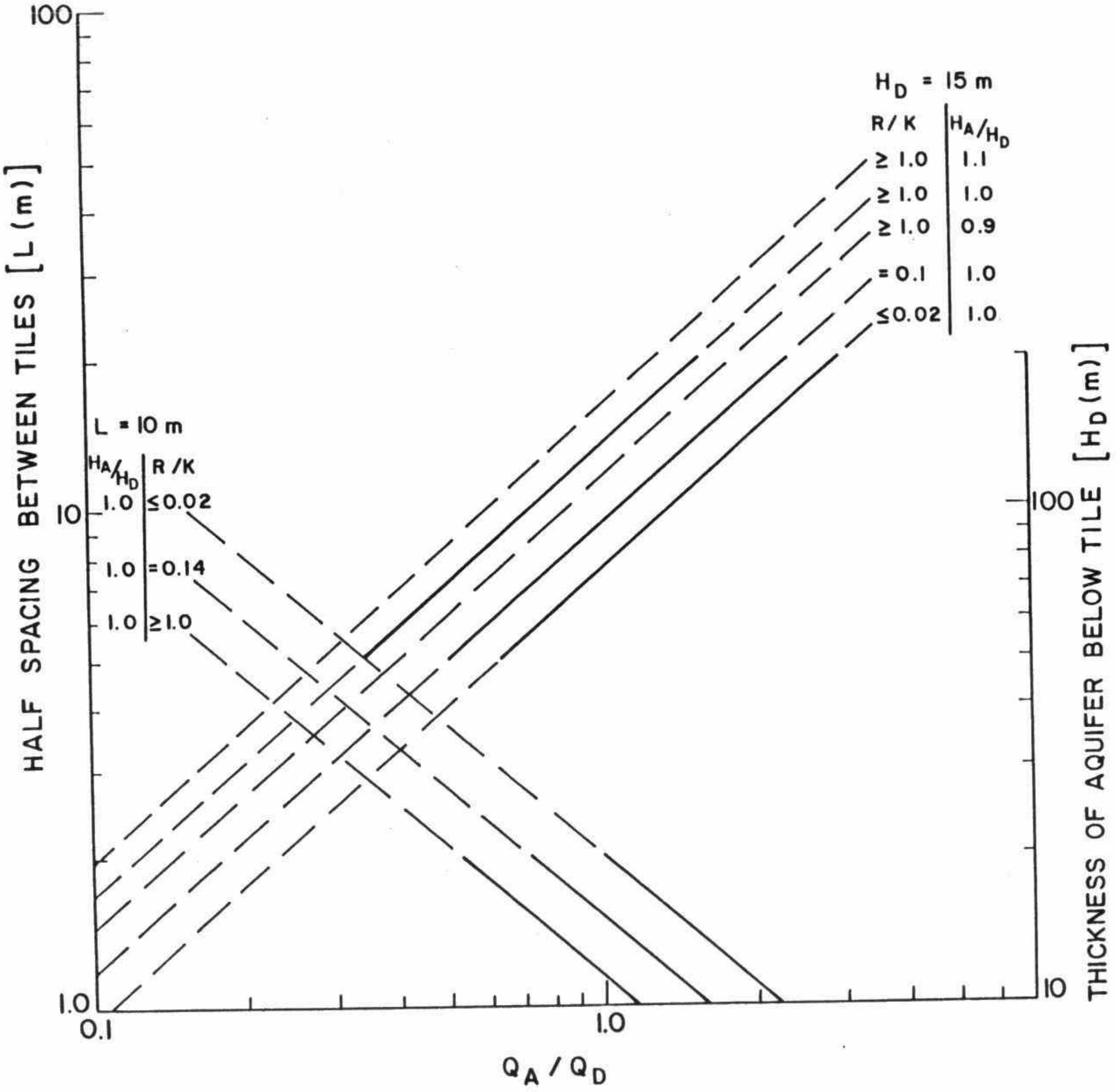

Figure 7. Graph showing relationship between drain performance, half spacing between tiles and thickness of aquifer below tile, for specified ranges in hydraulic conditions and head ratios.

CONCLUSIONS

The suitability of tile drains to capture landfill leachate is primarily dependent on the hydraulic conditions within the aquifer in which the landfill is placed and particularly on the vertical gradients. Recharge rate and hydraulic conductivity also exert a strong influence on performance. The results of this study indicate that if the hydraulic head at the tiles is greater than at a deeper aquifer, then the tiles will perform poorly as interceptors of leachate. It seems, therefore, that for tile drains to be suitable for leachate collection, at least in systems similar to those considered in this study, the hydraulic conditions must be such that the tiles can be installed below the equipotential surface of a deeper aquifer or zone of interest. If the tiles are placed deeper than required by this condition, excess water will be drained by the tiles. Optimum drainage conditions are attained when all leachate is collected with a minimum infiltration of excess water. If the head relationships are changed by drainage to the tiles or other landfill operations, then any analysis made on the original conditions will not be valid.

The performance of a tile collector system is dependent on several factors including the ratio of recharge rate to saturated hydraulic conductivity, the spacing of the tiles and the thickness of the flow system considered below the level of the tiles. Increasing the level of the tiles above the datum level and decreasing the tile spacing have the effect of increasing the fraction of the leachate collected by the tiles.

In interpreting the above results, it must be remembered that these apply only to the case where the system is underlain by an aquifer whose head is unaffected by the tile bed. A change in the boundary conditions at depth can be expected to produce a different response of the collection system.

We have studied through numerical simulations a relatively simple system and the generality of our observations and interpretations have to be established by further studies. However, our results serve to identify some of the important parameters that govern the suitability and performance of tile drains as interceptors of landfill leachate. We believe our procedure for analyzing the effectiveness of tiles at a specific site offers great promise for optimizing the design of tile systems for leachate collection. We plan to extend the study to use the same approach to examine situations occurring in the field.

Also, further studies will extend the application of the procedure to more general cases, by broadening the range of the previously defined parameters and by considering alternative boundary conditions at depth. Other parameters will be introduced to take into account the effect of field particularities such as occurrence of anisotropy and layering of soil hydraulic conductivities. This will lead to the evaluation of ways to artificially improve drainage by adding liners, gravel layers, or french drains to the leachate collection system.

In a final stage, changes in the boundary configuration limiting the half cell will be studied. These changes could be due to factors such as water table drop due to collection of leachate or lateral gradients produced by regional flow components.

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